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<p>(21) International Application Number: PCT/US89/04270 (22) International Filing Date: 29 September 1989 (29.09.89) (30) Priority data: 251,613 29 September 1988 (29.09.88) US (71) Applicant: CHEVRON RESEARCH COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventor: HARRISON, James, J. ; 12 Stonehaven Court, Novato, CA 94947 (US). (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i></p>
<p>(54) Title: NOVEL POLYMERIC DISPERSANTS HAVING ALTERNATING POLYALKYLENE AND SUCCINIC GROUPS</p> <p>(57) Abstract.</p> <p>Novel copolymers of unsaturated acidic reactants and high molecular weight olefins wherein at least 20 percent of the total high molecular weight olefin comprises the alkylvinylidene isomer are useful as dispersants in lubricating oils and fuels and also may be used to prepare polysuccinimides and other post-treated additives useful in lubricating oils and fuels.</p> <div data-bbox="1655 1582 2018 2601"> </div>		

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01 NOVEL POLYMERIC DISPERSANTS HAVING ALTERNATING
02 POLYALKYLENE AND SUCCINIC GROUPS

03

04 BACKGROUND OF THE INVENTION

05

06 The present invention relates to compositions which are
07 useful as intermediates for dispersants used in lubricating
08 oil compositions or as dispersants themselves. In addition,
09 some of these compositions are useful in the preparation of
10 novel high molecular weight dispersants which have superior
11 dispersant properties for dispersing sludge and varnish and
12 superior Viton Seal compatibility.

13

14 The high molecular weight dispersants of the present
15 invention also advantageously impart fluidity modifying
16 properties to lubricating oil compositions which are suffi-
17 cient to allow elimination of some proportion of viscosity
18 index improver from multigrade lubricating oil compositions
19 which contain these dispersants.

20

21 Alkenyl-substituted succinic anhydrides have been used as
22 dispersants. Such alkenyl-substituted succinic anhydrides
23 have been prepared by two different processes, a thermal
24 process (see, e.g., U.S. Patent No. 3,361,673) and a
25 chlorination process (see, e.g., U.S. Patent No. 3,172,892).
26 The polyisobutenyl succinic anhydride ("PIBSA") produced by
27 the thermal process has been characterized as a monomer
28 containing a double bond in the product. Although the exact
29 structure of chlorination PIBSA has not been definitively
30 determined, the chlorination process PIBAs have been charac-
31 terized as monomers containing either a double bond, a ring,
32 other than a succinic anhydride ring and/or chlorine in the
33 product. [See J. Weill and B. Sillion, "Reaction of
34 Chlorinated Polyisobutene with Maleic Anhydride: Mechanism

2

01 Catalysis by Dichloromaleic Anhydride", Revue de l'Institut
02 Français du Pétrole, Vol. 40, No. 1, pp. 77-89
03 (January-February, 1985).] Such compositions include
04 one-to-one monomeric adducts (see, e.g., U.S. Patents
05 Nos. 3,219,666; 3,381,022) as well as adducts having poly-
06 alkenyl-derived substituents adducted with at least 1.3
07 succinic groups per polyalkenyl-derived substituent (see,
08 e.g., U.S. Patent No. 4,234,435).

09
10 In addition, copolymers of maleic anhydrides and some ali-
11 phatic alpha-olefins have been prepared. The polymers so
12 produced were useful for a variety of purposes including
13 dispersants for pigments and intermediates in the prepara-
14 tion of polyesters by their reaction with polyols or poly-
15 epoxides. However, olefins having more than about 30 carbon
16 atoms were found to be relatively unreactive. (See, e.g.,
17 U.S. Patents Nos. 3,461,108; 3,560,455; 3,560,456;
18 3,560,457; 3,580,893; 3,706,704; 3,729,450; and 3,729,451).

19
20 SUMMARY OF THE INVENTION

21
22 The present invention is directed to novel compositions
23 useful as additives which comprise copolymers of an unsatu-
24 rated acidic reactant and high molecular weight olefin
25 wherein at least about 20 percent of the total high
26 molecular weight olefin comprises the alkylvinylidene
27 isomer, said copolymers having alternating succinic and
28 polyalkyl groups. The high molecular weight olefin has a
29 sufficient number of carbon atoms such that the resulting
30 copolymer is soluble in lubricating oil. Suitable olefins
31 include those having about 32 carbon atoms or more (prefer-
32 ably having about 52 carbon atoms or more). Those preferred
33 high molecular weight olefins include polyisobutenes.
34 Especially preferred are polyisobutenes having average

3

01 molecular weights of from about 500 to about 5000 and in
02 which the alkylvinylidene isomer comprises at least 50
03 percent of the total olefin.

04

05 These copolymers are useful as dispersants themselves and
06 also as intermediates in the preparation of other dispersant
07 additives having improved dispersancy and/or detergency
08 properties when employed in a lubricating oil.

09

10 These copolymers are also advantageous because they do not
11 contain double bonds, rings, other than succinic anhydride
12 rings, or chlorine (in contrast to thermal and chlorination
13 PIBSAs) and as such have improved stability, as well as
14 improved environmental properties due to the absence of
15 chlorine.

16

17 The present invention is also directed to polysuccinimides
18 which are prepared by reacting a copolymer of the present
19 invention with a polyamine to give a polysuccinimide. The
20 present invention is directed to mono-polysuccinimides
21 (where a polyamine component reacts with one succinic
22 group); bis-polysuccinimides (where a polyamine component
23 reacts with a succinic group from each of two copolymer
24 molecules, thus effectively cross-linking the copolymer
25 molecules); and higher polysuccinimides (where a polyamine
26 component reacts with a succinic group from each of greater
27 than 2 copolymer molecules). These polysuccinimides are
28 useful as dispersants and/or detergents in fuels and oils.
29 In addition, these polysuccinimides have advantageous vis-
30 cosity modifying properties, and may provide a viscosity
31 index credit ("V.I. Credit") when used in lubricating oils,
32 which may permit elimination of some portion of viscosity
33 index improver ("V.I. Improver") from multigrade lubricating
34 oils containing the same.

4

01 In addition, the polysuccinimides of the present invention
02 can form a ladder polymeric structure or a cross-linked
03 polymeric structure. These structures are advantageous
04 because it is believed such structures are more stable and
05 resistant to hydrolytic degradation and also to degradation
06 by shear stress.

07
08 In addition, the present invention is directed to modified
09 polysuccinimides wherein one or more of the nitrogens of the
10 polyamine component is substituted with a hydrocarbyl oxy-
11 carbonyl, a hydroxyhydrocarbyl oxycarbonyl or a hydroxy
12 poly(oxyalkylene)-oxycarbonyl. These modified polysuccini-
13 mides are improved dispersants and/or detergents for use in
14 fuels or oils.

15
16 Accordingly, the present invention also relates to a lubri-
17 cating oil composition comprising a major amount of an oil
18 of lubricating viscosity and an amount of a copolymer,
19 polysuccinimide or modified succinimide additive of the
20 present invention sufficient to provide dispersancy and/or
21 detergency. The additives of the present invention may also
22 be formulated in lubricating oil concentrates which comprise
23 from about 90 to about 50 weight percent of an oil of lubri-
24 cating viscosity and from about 10 to about 50 weight
25 percent of an additive of the present invention.

26
27 Another composition aspect of the present invention is a
28 fuel composition comprising a major portion of a fuel
29 boiling in a gasoline or diesel range and an amount of
30 copolymer, polysuccinimide or modified succinimide additives
31 sufficient to provide dispersancy and/or detergency. The
32 present invention is also directed to fuel concentrates
33 comprising an inert stable oleophilic organic solvent
34 boiling in the range of about 150°F to about 400°F and from

5

01 about 5 to about 50 weight percent of an additive of the
02 present invention.

03

04 Definitions

05

06 As used herein, the following terms have the following
07 meanings unless expressly stated to the contrary.

08

09 The term "unsaturated acidic reactants" refers to maleic or
10 fumaric reactants of the general formula:

11

12

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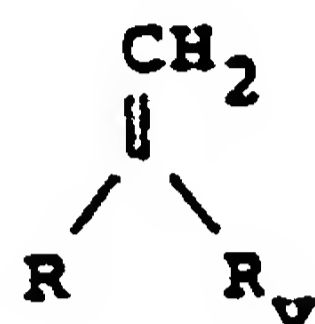


14

15 wherein X and X' are the same or different, provided that at
16 least one of X and X' is a group that is capable of reacting
17 to esterify alcohols, form amides or amine salts with ammo-
18 nia or amines, form metal salts with reactive metals or
19 basically reacting metal compounds and otherwise function as
20 acylating agents. Typically, X and/or X' is -OH, -O-hydro-
21 carbyl, -OM⁺ where M⁺ represents one equivalent of a metal,
22 ammonium or amine cation, -NH₂, -Cl, -Br, and taken together
23 X and X' can be -O- so as to form an anhydride. Preferably
24 X and X' are such that both carboxylic functions can enter
25 into acylation reactions. Maleic anhydride is a preferred
26 unsaturated acidic reactant. Other suitable unsaturated
27 acidic reactants include electron-deficient olefins such as
28 monophenyl maleic anhydride; monomethyl, dimethyl, mono-
29 chloro, monobromo, monofluoro, dichloro and difluoro maleic
30 anhydride; N-phenyl maleimide and other substituted
31 maleimides; isomaleimides; fumaric acid, maleic acid, alkyl
32 hydrogen maleates and fumarates, dialkyl fumarates and
33 maleates, fumaronilic acids and maleanic acids; and
34 maleonitrile, and fumaronitrile.

6

01 The term "alkylvinylidene" or "alkylvinylidene isomer"
02 refers to high molecular weight olefins and polyalkylene
03 components having the following vinylidene structure



(III)

04
05
06
07
08 wherein R is alkyl or substituted alkyl of sufficient chain
09 length to give the resulting molecule solubility in lubri-
10 cating oils and fuels, thus R generally has at least about
11 30 carbon atoms, preferably at least about 50 carbon atoms
12 and R_v is lower alkyl of about 1 to about 6 carbon atoms.
13

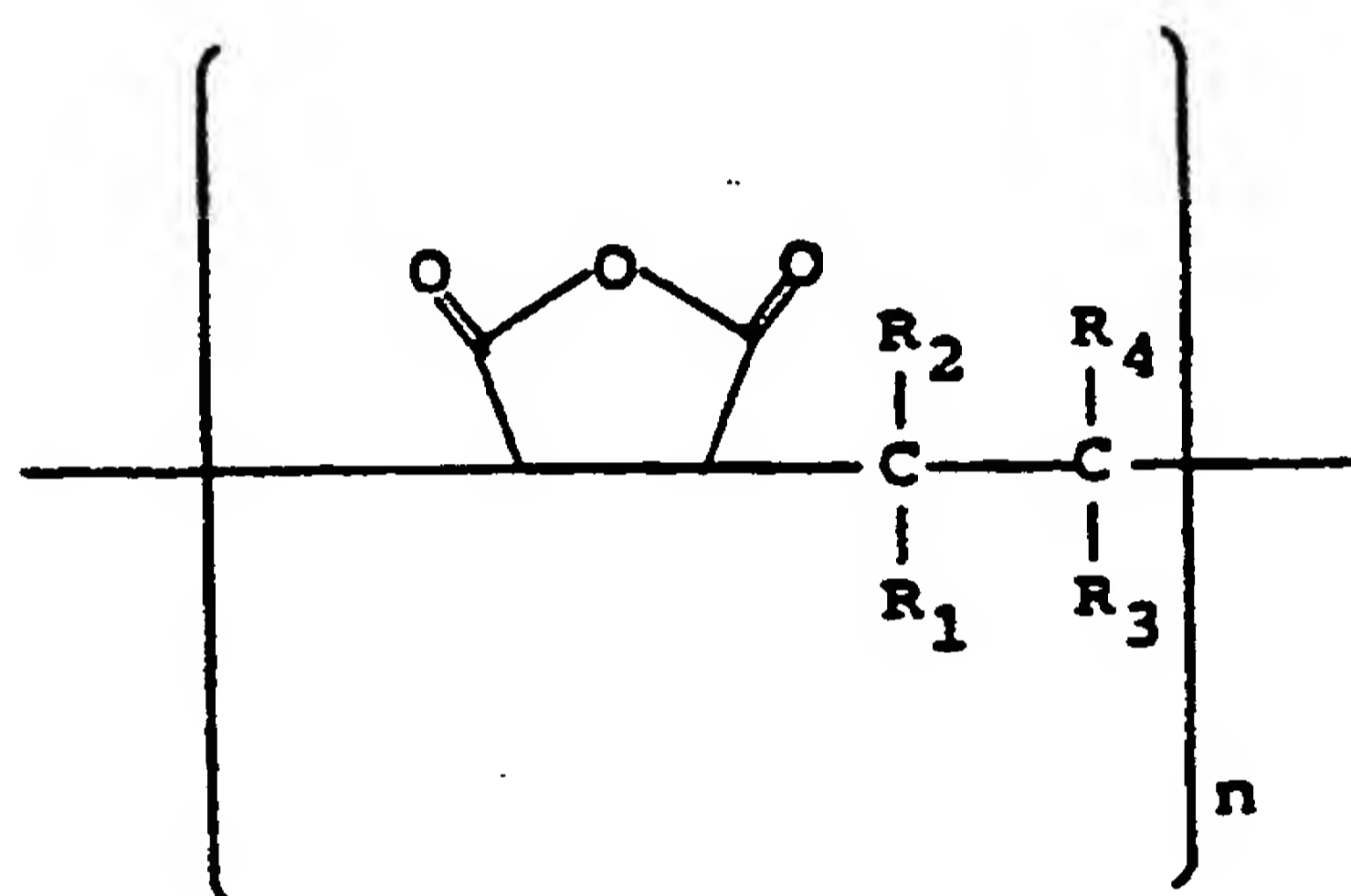
14 The term "soluble in lubricating oil" refers to the ability
15 of a material to dissolve in aliphatic and aromatic hydro-
16 carbons such as lubricating oils or fuels in essentially all
17 proportions.
18

19 The term "high molecular weight olefins" refers to olefins
20 (including polymerized olefins having a residual unsatura-
21 tion) of sufficient molecular weight and chain length to
22 lend solubility in lubricating oil to their reaction prod-
23 ucts. Typically olefins having about 32 carbons or greater
24 (preferably olefins having about 52 carbons or more)
25 suffice.
26

27 The term "high molecular weight polyalkyl" refers to poly-
28 alkyl groups of sufficient molecular weight and hydrocarbyl
29 chain length that the products prepared having such groups
30 are soluble in lubricating oil. Typically these high
31 molecular weight polyalkyl groups have at least about 30
32 carbon atoms, preferably at least about 50 carbon atoms.
33 These high molecular weight polyalkyl groups may be derived
34 from high molecular weight olefins.

01 The term "PIBSA" is an abbreviation for polyisobutenyl
 02 succinic anhydride.

03
 04 The term "polyPIBSA" refers to a class of copolymers within
 05 the scope of the present invention which are copolymers of
 06 polyisobutene and an unsaturated acidic reactant which have
 07 alternating succinic groups and polyisobutyl groups.
 08 PolyPIBSA has the general formula

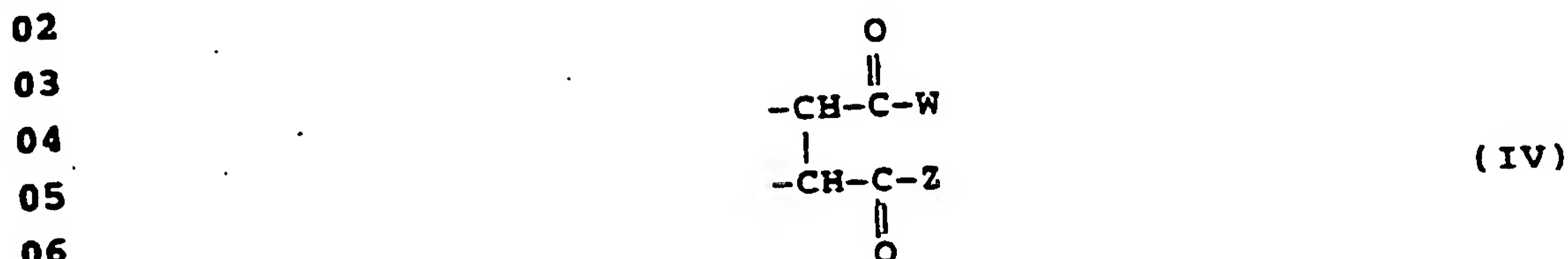


19 wherein n is one or greater; R_1 , R_2 , R_3 and R_4 are selected from
 20 hydrogen, methyl and polyisobutyl having at least about 30 carbon
 21 atoms (preferably at least about 50 carbon atoms) wherein either
 22 R_1 and R_2 are hydrogen and one of R_3 and R_4 is methyl and the
 23 other is polyisobutyl, or R_3 and R_4 are hydrogen and one of R_1
 24 and R_2 is methyl and the other is polyisobutyl.

25
 26 The term "PIBSA number" refers to the anhydride (succinic group)
 27 content of polyPIBSA on a 100% actives basis. The PIBSA number
 28 is calculated by dividing the saponification number by the
 29 percent polyPIBSA in the product. The units are mg KOH per gram
 30 sample.

31
 32
 33
 34

01 The term "succinic group" refers to a group having the formula



07

08 wherein W and Z are independently selected from the group

09 consisting of -OH, -Cl, -O- lower alkyl or taken together

10 are -O- to form a succinic anhydride group.

11

12 The term "degree of polymerization" expresses the length of

13 a linear polymer and refers to the number of repeating

14 (monomeric) units in the chain. The average molecular

15 weight of a polymer is the product of the degree of polymer-

16 ization and the average molecular weight of the repeating

17 unit (monomer). Accordingly, the average degree of poly-

18 merization is calculated by dividing the average molecular

19 weight of the polymer by the average molecular weight of the

20 repeating unit.

21

22 The term "polysuccinimide" refers to the reaction product of

23 a copolymer of the present invention with polyamine.

24

25 BRIEF DESCRIPTION OF THE DRAWING

26

27 FIG. 1 depicts one embodiment of a polysuccinimide of the

28 present invention, wherein R is polyisobutyl, R₁ is lower

29 alkyl, I is an initiator group and T is a terminator group.

30

31

32

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34

DETAILED DESCRIPTION OF THE INVENTIONA. COPOLYMER

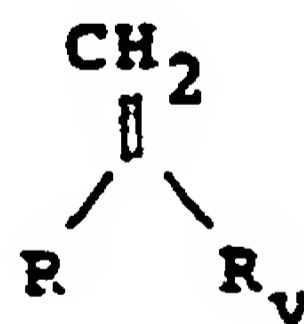
The copolymers of the present invention are prepared by reacting a high molecular weight olefin wherein at least about 20% of the total olefin composition comprises the alkylvinylidene isomer and an unsaturated acidic reactant in the presence of a free radical initiator. Suitable high molecular weight olefins have a sufficient number of carbon atoms so that the resulting copolymer is soluble in lubricating oil and thus have on the order of about 32 carbon atoms or more. Preferred high molecular weight of olefins are polyisobutenes and polypropylenes. Especially preferred are polyisobutenes, particularly preferred are those having a molecular weight of about 500 to about 5000, more preferably about 900 to about 2500. Preferred unsaturated acidic reactants include maleic anhydride.

Since the high molecular weight olefins used to prepare the copolymers of the present invention are generally mixtures of individual molecules of different molecular weights, individual copolymer molecules resulting will generally contain a mixture of high molecular weight polyalkyl groups of varying molecular weight. Also, mixtures of copolymer molecules having different degrees of polymerization will be produced.

The copolymers of the present invention have an average degree of polymerization of 1 or greater, preferably from about 1.1 to about 20, and more preferably from about 1.5 to about 10.

01 Among other factors, the present invention is based on my
02 surprising finding that the reaction of these high molecular
03 weight olefins wherein at least about 20% of the total
04 composition comprises the methylvinylidene isomer with an
05 unsaturated acidic reactant in the presence of a free
06 radical initiator results in a copolymer having alternating
07 polyalkylene and succinic groups. This is surprising in
08 view of the teachings that reaction of polyalkenes, such as
09 polyisobutenes, with unsaturated acidic reactants such as
10 maleic anhydride, in the presence of a free radical
11 initiator, resulted in a product similar to that produced by
12 the thermal process for PIBSA which is a monomeric
13 one-to-one adduct (see, e.g., U.S. Patent No. 3,367,864).
14 It was taught that high molecular weight olefins were rela-
15 tive unreactive under those conditions which was confirmed
16 by my findings that reaction of polyisobutene prepared using
17 AlCl_3 catalysis [in which the alkylvinylidene isomer com-
18 prised a very small proportion (less than about 10%) of the
19 total composition] with maleic anhydride in the presence of
20 a free radical initiator resulted in low yield of product.
21 In addition, the product obtained was similar to thermal
22 PIBSA in molecular weight.

23
24 Thus, the copolymers of the present invention are prepared
25 by reacting a "reactive" high molecular weight olefin in
26 which a high proportion of unsaturation, at least about 20%
27 is in the alkylvinylidene configuration, e.g.

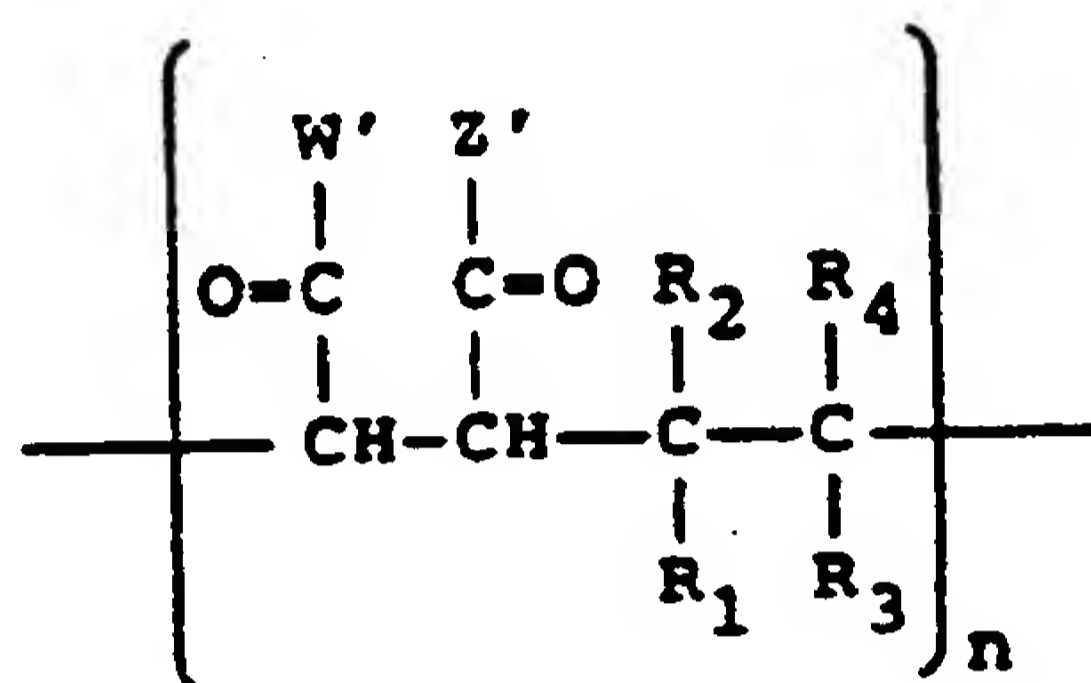


31
32 wherein R and R_v are as previously defined in conjunction
33 with Formula III, with an unsaturated acidic reactant in the
34 presence of a free radical initiator. The product copolymer

11

01 has alternating polyalkylene and succinic groups and has an
 02 average degree of polymerization of 1 or greater.

03
 04 The copolymers of the present invention have the general
 05 formula:

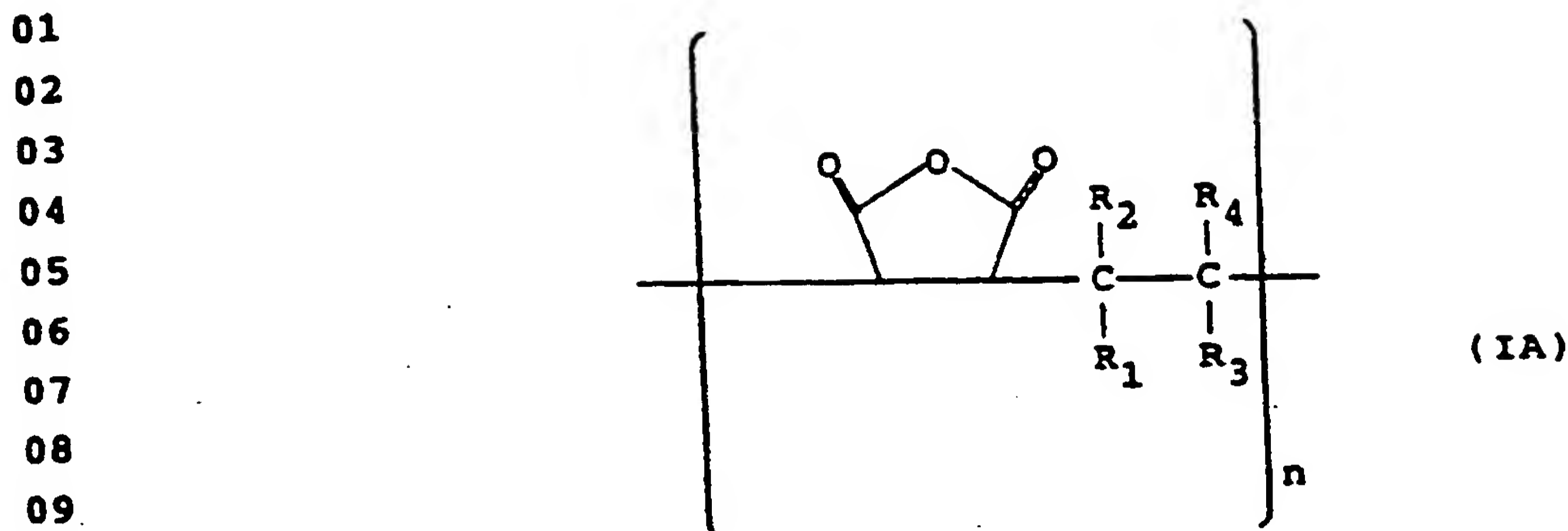


13
 14 wherein W' and Z' are independently selected from the group
 15 consisting of -OH, -O- lower alkyl or taken together are -O-
 16 to form a succinic anhydride group, n is one or greater; and
 17 R₁, R₂, R₃ and R₄ are selected from hydrogen, lower alkyl of
 18 1 to 6 carbon atoms, and high molecular weight polyalkyl
 19 wherein either R₁ and R₂ are hydrogen and one of R₃ and R₄
 20 is lower alkyl and the other is high molecular weight poly-
 21 alkyl, or R₃ and R₄ are hydrogen and one of R₁ and R₂ is
 22 lower alkyl and the other is high molecular weight
 23 polyalkyl.

24
 25 In a preferred embodiment, when maleic anhydride is used as
 26 the unsaturated acidic reactant, the reaction produces
 27 copolymers predominately of the following formula:

28
 29
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 31
 32
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 34

12

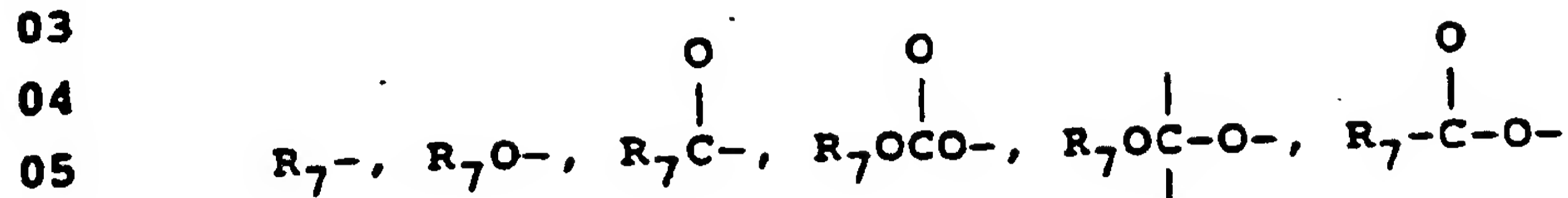


12 wherein n is about 1 to about 100, preferably about 2 to
13 about 20, more preferably 2 to 10, and R_1 , R_2 , R_3 and R_4 are
14 selected from hydrogen, lower alkyl of about 1 to 6 carbon
15 atoms and higher molecular weight polyalkyl, wherein either
16 R_1 and R_2 are hydrogen and one of R_3 and R_4 is lower alkyl
17 and the other is high molecular weight polyalkyl or R_3 and
18 R_4 are hydrogen and one of R_1 and R_2 is lower alkyl and the
19 other is high molecular weight polyalkyl.

20
21 Preferably, the high molecular weight polyalkyl group has at
22 least about 30 carbon atoms (preferably at least about 50
23 carbon atoms). Preferred high molecular weight polyalkyl
24 groups include polyisobutyl groups. Preferred polyisobutyl
25 groups include those having average molecular weights of
26 about 500 to about 5000, more preferably from about 900 to
27 about 2500. Preferred lower alkyl groups include methyl and
28 ethyl; especially preferred lower alkyl groups include
29 methyl.

30
31 Generally, such copolymers contain an initiator group, I,
32 and a terminator group, T, as a result of the reaction with
33 the free radical initiator used in the polymerization
34

01 reaction. In such a case, the initiator and terminator
 02 groups may be



06

07

08 where R_7 is hydrogen, alkyl, aryl, alkaryl, cycloalkyl,
 09 alkoxy, cycloalkoxy, acyl, alkenyl, cycloalkenyl, alkynyl;
 10 or alkyl, aryl or alkaryl optionally substituted with 1 to
 11 4 substituents independently selected from nitrile, keto,
 12 halogen, nitro, alkyl, aryl, and the like. Alternatively,
 13 the initiator group and/or terminator group may be derived
 14 from the reaction product of the initiator with another
 15 material such as solvent; for example, the initiator may
 16 react with toluene to produce a benzyl radical.

17

18 The copolymers of the present invention differ from the
 19 PIBSAs prepared by the thermal process in that the thermal
 20 process products contain a double bond and a singly substi-
 21 tuted succinic anhydride group. The copolymers of the
 22 present invention differ from the PIBSAs prepared by the
 23 chlorination process, since those products contain a double
 24 bond, a ring, other than a succinic anhydride ring or one or
 25 more chlorine atoms.

26

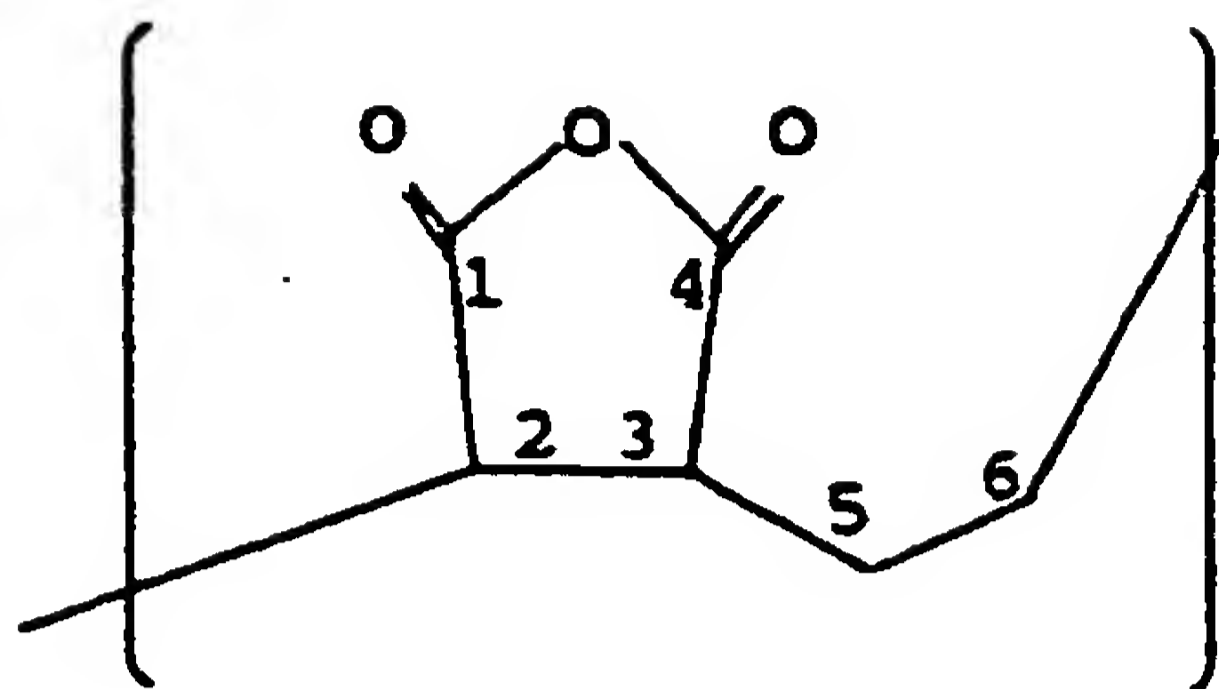
27 The copolymers of the present invention contain no double
 28 bonds, rings, other than succinic anhydride rings, or
 29 chlorine atoms. In addition, the succinic anhydride groups
 30 are doubly substituted (i.e., have two substituents, one of
 31 which may be hydrogen) at the 2- and 3-positions, that is:

32

33

34

14



A(1) High Molecular Weight Polyalkylene Group

The high molecular weight polyalkyl group is derived from a high molecular weight olefin. The high molecular weight olefins used in the preparation of the copolymers of the present invention are of sufficiently long chain length so that the resulting composition is soluble in and compatible with mineral oils, fuels and the like; and the alkylvinylidene isomer of the high molecular weight olefin comprises at least about 20% of the total olefin composition.

Such high molecular weight olefins are generally mixtures of molecules having different molecular weights and can have at least one branch per 6 carbon atoms along the chain, preferably at least one branch per 4 carbon atoms along the chain, and particularly preferred that there be about one branch per 2 carbon atoms along the chain. These branched chain olefins may conveniently comprise polyalkenes prepared by the polymerization of olefins of from 3 to 6 carbon atoms, and preferably from olefins of from 3 to 4 carbon atoms, and more preferably from propylene or isobutylene. The addition-polymerizable olefins employed are normally 1-olefins. The branch may be of from 1 to 4 carbon atoms, more usually of from 1 to 2 carbon atoms and preferably methyl.

15

01 The preferred alkylvinylidene isomer comprises a methyl- or
02 ethylvinylidene isomer, more preferably the methylvinylidene
03 isomer.

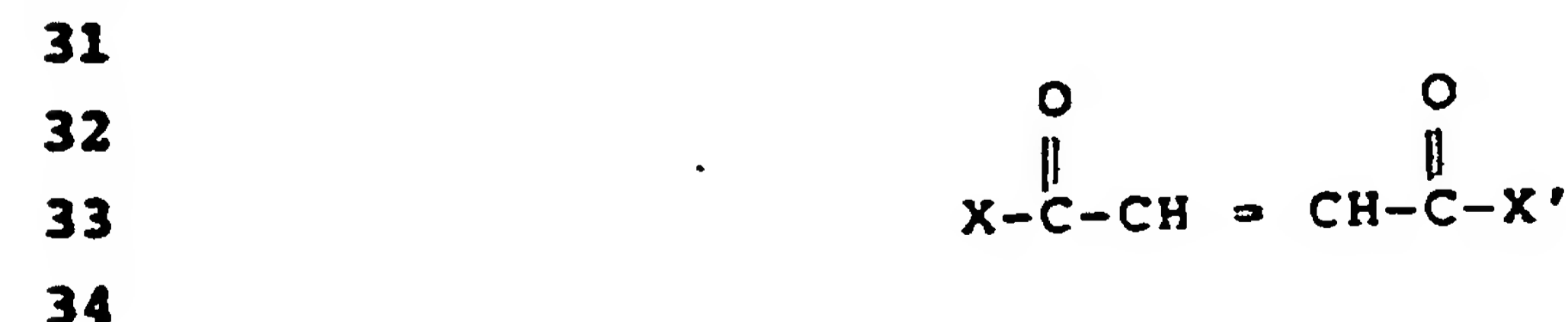
04
05 The especially preferred high molecular weight olefins used
06 to prepare the copolymers of the present invention are poly-
07 isobutenes which comprise at least about 20% of the more
08 reactive methylvinylidene isomer, preferably at least 50%
09 and more preferably at least 70%. Suitable polyisobutenes
10 include those prepared using BF_3 catalysis. The preparation
11 of such polyisobutenes in which the methylvinylidene isomer
12 comprises a high percentage of the total composition is
13 described in U.S. Patents Nos. 4,152,499 and 4,605,808.

14
15 Polyisobutenes produced by conventional AlCl_3 catalysis when
16 reacted with unsaturated acidic reactants, such as maleic
17 anhydride, in the presence of a free radical initiator,
18 produce products similar to thermal PIBSA in molecular
19 weight and thus do not produce a copolymeric product.

20
21 Preferred are polyisobutenes having average molecular
22 weights of about 500 to about 5000. Especially preferred
23 are those having average molecular weights of about 900 to
24 about 2500.

25
26 A(2) Unsaturated Acidic Reactant

27
28 The unsaturated acidic reactant used in the preparation of
29 the copolymers of the present invention comprises a maleic
30 or fumaric reactant of the general formula:



01 wherein X and X' are the same or different, provided that at
02 least one of X and X' is a group that is capable of reacting
03 to esterify alcohols, form amides or amine salts with ammo-
04 nia or amines, form metal salts with reactive metals or
05 basically reacting metal compounds and otherwise function to
06 acylate. Typically, X and/or X' is -OH, -O-hydrocarbyl,
07 -OM⁺ where M⁺ represents one equivalent of a metal, ammonium
08 or amine cation, -NH₂, -Cl, -Br, and taken together X and X'
09 can be -O- so as to form an anhydride. Preferably, X and X'
10 are such that both carboxylic functions can enter into
11 acylation reactions. Preferred are acidic reactants where X
12 and X' are each independently selected from the group con-
13 sisting of -OH, -Cl, -O- lower alkyl and when taken
14 together, X and X' are -O-. Maleic anhydride is the pre-
15 ferred acidic reactant. Other suitable acidic reactants
16 include electron-deficient olefins such as monophenyl maleic
17 anhydride; monomethyl, dimethyl, monochloro, monobromo,
18 monofluoro, dichloro and difluoro maleic anhydride; N-phenyl
19 maleimide and other substituted maleimides; isomaleimides;
20 fumaric acid, maleic acid, alkyl hydrogen maleates and
21 fumarates, dialkyl fumarates and maleates, fumaronilic acids
22 and maleanic acids; and maleonitrile, and fumaronitrile.
23
24 Preferred unsaturated acidic reactants include maleic
25 anhydride, and maleic acid. The particularly preferred
26 acidic reactant is maleic anhydride.

27 A(3) General Preparation of Copolymer

28
29
30 As noted above, the copolymers of the present invention are
31 prepared by reacting a reactive high molecular weight olefin
32 and an unsaturated acidic reactant in the presence of a free
33 radical initiator.
34

01 The reaction may be conducted at a temperature of about
02 -30°C to about 210°C, preferably from about 40°C to about
03 150°C. I have found that degree of polymerization is
04 inversely proportional to temperature. Accordingly, for the
05 preferred high molecular weight copolymers, it is advan-
06 tageous to employ lower reaction temperatures. For example,
07 if the reaction is conducted at about 138°C, an average
08 degree of polymerization of about 1.3 was obtained. How-
09 ever, if the reaction was conducted at a temperature of
10 about 40°C, an average degree of polymerization of about
11 10.5 was obtained.

12
13 The reaction may be conducted neat, that is, both the high
14 molecular weight olefin, and acidic reactant and the free
15 radical initiator are combined in the proper ratio, and then
16 stirred at the reaction temperature.

17
18 Alternatively, the reaction may be conducted in a diluent.
19 For example, the reactants may be combined in a solvent.
20 Suitable solvents include those in which the reactants and
21 free radical initiator are soluble and include acetone,
22 tetrahydrofuran, chloroform, methylene chloride, dichloro-
23 ethane, toluene, dioxane, chlorobenzene, xylenes, or the
24 like. After the reaction is complete, volatile components
25 may be stripped off. When a diluent is employed, it is
26 preferably inert to the reactants and products formed and is
27 generally used in an amount sufficient to ensure efficient
28 stirring.

29
30 Moreover, my colleague W. R. Ruhe, has discovered that in
31 the preparation of polyPIBSA, improved results are obtained
32 by using PIBSA or polyPIBSA as a solvent for the reaction.
33 (See, e.g., Examples 16, 17A and 17B herein.)

34

01 In general, the copolymerization can be initiated by any
02 free radical initiator. Such initiators are well known in
03 the art. However, the choice of free radical initiator may
04 be influenced by the reaction temperature employed.

05
06 The preferred free-radical initiators are the peroxide-type
07 polymerization initiators and the azo-type polymerization
08 initiators. Radiation can also be used to initiate the
09 reaction, if desired.

10
11 The peroxide-type free-radical initiator can be organic or
12 inorganic, the organic having the general formula: R_3OOR_3'
13 where R_3 is any organic radical and R_3' is selected from the
14 group consisting of hydrogen and any organic radical. Both
15 R_3 and R_3' can be organic radicals, preferably hydrocarbon,
16 aroyl, and acyl radicals, carrying, if desired, substituents
17 such as halogens, etc. Preferred peroxides include
18 di-tert-butyl peroxide, tert-butyl peroxybenzoate, and
19 dicumyl peroxide.

20
21 Examples of other suitable peroxides, which in no way are
22 limiting, include benzoyl peroxide; lauroyl peroxide; other
23 tertiary butyl peroxides; 2,4-dichlorobenzoyl peroxide;
24 tertiary butyl hydroperoxide; cumene hydroperoxide; diacetyl
25 peroxide; acetyl hydroperoxide; diethylperoxycarbonate;
26 tertiary butyl perbenzoate; and the like.

27
28 The azo-type compounds, typified by alpha,alpha'-azo-
29 bisisobutyronitrile, are also well-known free-radical
30 promoting materials. These azo compounds can be defined as
31 those having present in the molecule group $-N=N$ wherein the
32 balances are satisfied by organic radicals, at least one of
33 which is preferably attached to a tertiary carbon. Other
34 suitable azo compounds include, but are not limited to,

01 p-bromobenzenediazonium fluoborate; p-tolyldiazoaminoben-
02 zene; p-bromobenzenediazonium hydroxide; azomethane and
03 phenyldiazonium halides. A suitable list of azo-type com-
04 pounds can be found in U.S. Patent No. 2,551,813, issued
05 May 8, 1951 to Paul Pinkney.

06

07 The amount of initiator to employ, exclusive of radiation,
08 of course, depends to a large extent on the particular
09 initiator chose, the high molecular olefin used and the
10 reaction conditions. The initiator must, of course, be
11 soluble in the reaction medium. The usual concentrations of
12 initiator are between 0.001:1 and 0.2:1 moles of initiator
13 per mole of acidic reactant, with preferred amounts between
14 0.005:1 and 0.10:1.

15

16 The polymerization temperature must be sufficiently high to
17 break down the initiator to produce the desired free-radi-
18 cals. For example, using benzoyl peroxide as the initiator,
19 the reaction temperature can be between about 75°C and about
20 90°C, preferably between about 80°C and about 85°C. Higher
21 and lower temperatures can be employed, a suitable broad
22 range of temperatures being between about 20°C and about
23 200°C, with preferred temperatures between about 50°C and
24 about 150°C.

25

26 The reaction pressure should be sufficient to maintain the
27 solvent in the liquid phase. Pressures can therefore vary
28 between about atmospheric and 100 psig or higher, but the
29 preferred pressure is atmospheric.

30

31 The reaction time is usually sufficient to result in the
32 substantially complete conversion of the acidic reactant and
33 high molecular weight olefin to copolymer. The reaction

34

01 time is suitable between one and 24 hours, with preferred
02 reaction times between two and ten hours.

03

04 As noted above, the subject reaction is a solution-type
05 polymerization reaction. The high molecular weight olefin,
06 acidic reactant, solvent and initiator can be brought
07 together in any suitable manner. The important factors are
08 intimate contact of the high molecular weight olefin and
09 acidic reactant in the presence of a free-radical producing
10 material. The reaction, for example, can be conducted in a
11 batch system where the high molecular weight olefin is added
12 all initially to a mixture of acidic reactant, initiator and
13 solvent or the high molecular weight olefin can be added
14 intermittently or continuously to the reaction pot. Alter-
15 natively, the reactants may be combined in other orders; for
16 example, acidic reactant and initiator may be added to high
17 molecular weight olefin and solvent in the reaction pot. In
18 another manner, the components in the reaction mixture can
19 be added continuously to a stirred reactor with continuous
20 removal of a portion of the product to a recovery train or
21 to other reactors in series. The reaction can also suit-
22 ably take place in a coil-type reactor where the components
23 are added at one or more points along the coil.

24

25 In one envisioned embodiment, the reaction product of an
26 unsaturated acidic reactant and a high molecular weight,
27 high vinylidene-containing olefin is further reacted
28 thermally. In this embodiment, any unreacted olefin,
29 generally the more hindered olefins, i.e., the non-vinyl-
30 idene, that do not react readily with the unsaturated acidic
31 reactant under free radical conditions are reacted with
32 unsaturated acidic reactant under thermal conditions, i.e.,
33 at temperatures of about 180° to 280°C. These conditions

34

21

01 are similar to those used for preparing thermal process
02 PIBSA.

03

04 The reaction solvent, as noted above, must be one which
05 dissolves both the acidic reactant and the high molecular
06 weight olefin. It is necessary to dissolve the acidic
07 reactant and high molecular weight olefin so as to bring
08 them into intimate contact in the solution polymerization
09 reaction. It has been found that the solvent must also be
10 one in which the resultant copolymers are soluble.

11

12 Suitable solvents include liquid saturated or aromatic
13 hydrocarbons having from six to 20 carbon atoms; ketones
14 having from three to five carbon atoms; and liquid saturated
15 aliphatic dihalogenated hydrocarbons having from one to five
16 carbon atoms per molecule, preferably from one to three car-
17 bon atoms per molecule. By "liquid" is meant liquid under
18 the conditions of polymerization. In the dihalogenated
19 hydrocarbons, the halogens are preferably on adjacent carbon
20 atoms. By "halogen" is meant F, Cl and Br. The amount of
21 solvent must be such that it can dissolve the acidic reac-
22 tant and high molecular weight olefin in addition to the
23 resulting copolymers. The volume ratio of solvent to high
24 molecular weight olefin is suitably between 1:1 and 100:1
25 and is preferably between 1.5:1 and 4:1.

26

27 Suitable solvents include the ketones having from three to
28 six carbon atoms and the saturated dichlorinated hydro-
29 carbons having from one to five, more preferably one to
30 three, carbon atoms.

31

32 Examples of suitable solvents include, but are not limited,
33 to:

34

22

- 01 1. ketones, such as: acetone; methylethylketone;
02 diethylketone; and methylisobutylketone;
03
04 2. aromatic hydrocarbons, such as: benzene; xylene; and
05 toluene;
06
07 3. saturated dihalogenated hydrocarbons, such as:
08 dichloromethane; dibromomethane; 1-bromo-2-chloroethane;
09 1,1-dibromoethane; 1,1-dichloroethane;
10 1,2-dichloroethane; 1,3-dibromopropane;
11 1,2-dibromopropane; 1,2-dibromo-2-methylpropane;
12 1,2-dichloropropane; 1,1-dichloropropane;
13 1,3-dichloropropane; 1-bromo-2-chloropropane;
14 1,2-dichlorobutane; 1,5-dibromopentane; and
15 1,5-dichloropentane; or
16
17 4. mixtures of the above, such as: benzene-
18 methylethylketone.
19
20 As noted previously, W. R. Ruhe has discovered that use of a
21 mixture of copolymer and polyisobutene as a solvent results
22 in improved yields and advantageously dissolves the acidic
23 reactant when used as a reaction medium.
24
25 The copolymer is conveniently separated from solvent and
26 unreacted acidic reactant by conventional procedures such as
27 phase separation, solvent distillation, precipitation and
28 the like. If desired, dispersing agents and/or cosolvents
29 may be used during the reaction.
30
31 The isolated copolymer may then be reacted with a polyamine
32 to form a polymeric succinimide. The preparation and
33
34

23

01 characterization of such polysuccinimides and their treat-
02 ment with other agents to give other dispersant compositions
03 is described herein.

04

05

A(4) Preferred Copolymers

06

07 Preferred copolymers include those where an unsaturated
08 acidic reactant, most preferably maleic anhydride, is
09 copolymerized with a "reactive" polyisobutene, in which at
10 least about 50 percent or more of the polyisobutene com-
11 prises the alkylvinylidene, more preferably, the methyl-
12 vinylidene, isomer, to give a "polyPIBSA".

13

14 Preferred are polyPIBSAs wherein the polyisobutyl group has
15 an average molecular weight of about 500 to about 5000, more
16 preferably from about 950 to about 2500. Preferred are
17 polyPIBSAs having an average degree of polymerization of
18 about 1.1 to about 20, more preferably from about 1.5 to
19 about 10.

20

21

B. POLYSUCCINIMIDES

22

23 The polyamino polysuccinimides of the present invention are
24 prepared by reacting a copolymer of the present invention
25 with a polyamine. Polysuccinimides which may be prepared
26 include monopolysuccinimides (where a polyamine component
27 reacts with one succinic group), bis-polysuccinimides (where
28 a polyamine component reacts with a succinic group from each
29 of two copolymer molecules), higher succinimides (where a
30 polyamine component reacts with a succinic group from each
31 of more than 2 copolymer molecules) or mixtures thereof.

32 The polysuccinimide(s) produced may depend on the charge
33 mole ratio of polyamine to succinic groups in the copolymer
34 molecule and the particular polyamine used. Using a charge

24

01 mole ratio of polyamine to succinic groups in copolymer of
02 about 1.0, predominately monopolysuccinimide is obtained.
03 Charge mole ratios of polyamine to succinic group in copoly-
04 mer of about 1:2 may produce predominately bis-polysucci-
05 nimide. Higher polysuccinimides may be produced if there is
06 branching in the polyamine so that it may react with a
07 succinic group from each of greater than 2 copolymer
08 molecules.

09

10

B(1) Preferred Copolymers

11

12 Preferred copolymers include polyPIBSAs prepared according
13 to the present invention as described hereinabove.

14

15 Preferred polyPIBSAs include those prepared using a poly-
16 isobutene of average molecular weight of about 500 to about
17 5000, preferably of about 950 to about 2500 and wherein at
18 least about 50 percent of the total polyisobutene comprises
19 the alkylvinylidene isomer. Preferred alkylvinylidene
20 isomers include methylvinylidene and ethylvinylidene.
21 Especially preferred is methylvinylidene. Preferred are
22 polyPIBSAs having an average degree of polymerization of
23 about 1.1 to about 15. Particularly preferred polyPIBSAs
24 have an average degree of polymerization of about 1.5 to
25 about 10, and which are prepared using a polyisobutene
26 having an average molecular weight of about 900 to about
27 2500.

28

29

B(2) Polyamine

30

31 The polyamine employed to prepare the polyamino poly-
32 succinimides is preferably polyamine having from 2 to about
33 12 amine nitrogen atoms and from 2 to about 40 carbon atoms.
34 The polyamine is reacted with polyPIBSA to produce the poly-

25

01 amino polysuccinimide, employed in this invention. The
02 polyamine is so selected so as to provide at least one basic
03 amine per succinimide group. Since the reaction of a
04 nitrogen of a polyamino polysuccinimide to form a hydro-
05 carbyl oxycarbonyl, a hydroxy hydrocarbyl oxycarbonyl or a
06 hydroxy polyoxyalkylene oxycarbonyl is believed to effi-
07 ciently proceed through a secondary or primary amine, at
08 least one of the basic amine atoms of the polyamino poly-
09 succinimide must either be a primary amine or a secondary
10 amine. Accordingly, in those instances in which the
11 succinimide group contains only one basic amine, that amine
12 must either be a primary amine or a secondary amine. The
13 polyamine preferably has a carbon-to-nitrogen ratio of from
14 about 1:1 to about 10:1.

15
16 The polyamine portion of the polyamino polysuccinimide may
17 be substituted with substituents selected from (a) hydrogen,
18 (b) hydrocarbyl groups of from 1 to about 10 carbon atoms,
19 (c) acyl groups of from 2 to about 10 carbon atoms, and
20 (d) monoketo, monohydroxy, mononitro, monocyano, lower alkyl
21 and lower alkoxy derivatives of (b) and (c). "Lower", as
22 used in terms like "lower alkyl" or "lower alkoxy", means a
23 group containing from 1 to about 6 carbon atoms. At least
24 one of the substituents on one of the amines of the
25 polyamine is hydrogen, e.g., at least one of the basic
26 nitrogen atoms of the polyamine is a primary or secondary
27 amino nitrogen atom.

28
29 Hydrocarbyl, as used in describing the polyamine components
30 of this invention, denotes an organic radical composed of
31 carbon and hydrogen which may be aliphatic, alicyclic,
32 aromatic or combinations thereof, e.g., aralkyl. Prefer-
33 ably, the hydrocarbyl group will be relatively free of
34 aliphatic unsaturation, i.e., ethylenic and acetylenic,

26

01 particularly acetylenic unsaturation. The substituted
02 polyamines of the present invention are generally, but not
03 necessarily, N-substituted polyamines. Exemplary hydro-
04 carbyl groups and substituted hydrocarbyl groups include
05 alkyls such as methyl, ethyl, propyl, butyl, isobutyl,
06 pentyl, hexyl, octyl, etc., alkenyls such as propenyl,
07 isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls, such as
08 2-hydroxyethyl, 3-hydroxypropyl, hydroxyisopropyl,
09 4-hydroxybutyl, etc. ketoalkyls, such as 2-ketopropyl,
10 6-ketooctyl, etc., alkoxy and lower alkenoxy alkyls, such as
11 ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl,
12 2-(2-ethoxyethoxy)ethyl, 2-(2-(2-ethoxy-ethoxy)ethoxy)ethyl,
13 3,6,9,12-tetraoxatetradecyl, 2-(2-ethoxyethoxy)hexyl, etc.
14 The acyl groups of the aforementioned (c) substituents are
15 such as propionyl, acetyl, etc. The more preferred substit-
16 uents are hydrogen, C₁-C₆ alkyls and C₁-C₆ hydroxyalkyls.

17
18 In a substituted polyamine the substituents are found at any
19 atom capable of receiving them. The substituted atoms,
20 e.g., substituted nitrogen atoms, are generally geometri-
21 cally inequivalent, and consequently the substituted amines
22 finding use in the present invention can be mixtures of
23 mono- and polysubstituted polyamines with substituent groups
24 situated at equivalent and/or inequivalent atoms.

25
26 The more preferred polyamine finding use within the scope of
27 the present invention is a polyalkylene polyamine, including
28 alkylene diamine, and including substituted polyamines,
29 e.g., alkyl substituted polyalkylene polyamine. Preferably,
30 the alkylene group contains from 2 to 6 carbon atoms, there
31 being preferably from 2 to 3 carbon atoms between the
32 nitrogen atoms. Such groups are exemplified by ethylene,
33 1,2-propylene, 2,2-dimethylpropylene, trimethylene, etc.
34 Examples of such polyamines include ethylene diamine,

27

01 diethylene triamine, di(trimethylene)triamine, dipropylene
02 triamine, triethylene tetramine, tripropylene tetramine,
03 tetraethylene pentamine, and pentaethylene hexamine. Such
04 amines encompass isomers such as branched-chain polyamine
05 and the previously mentioned substituted polyamines,
06 including hydrocarbyl-substituted polyamines. Among the
07 polyalkylene polyamines, those containing 2-12 amine
08 nitrogen atoms and 2-24 carbon atoms are especially
09 preferred, and the C₂-C₅ alkylene polyamines are most
10 preferred, in particular, the lower polyalkylene polyamines,
11 e.g., ethylene diamine, dipropylene triamine, etc.

12
13 Preferred polyamines also include heavy polyamines such as
14 polyamine HPA available from Union Carbide.

15
16 The polyamine component also may contain heterocyclic poly-
17 amines, heterocyclic substituted amines and substituted
18 heterocyclic compounds, wherein the heterocycle comprises
19 one or more 5 to 6-membered rings containing oxygen and/or
20 nitrogen. Such heterocycles may be saturated or unsaturated
21 and substituted with groups selected from the aforementioned
22 (a), (b), (c) and (d). The heterocycles are exemplified by
23 piperazines, such as 2-methylpiperazine, N-(2-hydroxyethyl)-
24 piperazine, 1,2-bis-(n-piperazinyl)ethane, and N,N'-bis(N-
25 piperazinyl)piperazine, 2-methylimidazoline, 3-amino-
26 piperidine, 2-aminopyridine, 2-(3-aminoethyl)-3-pyrroline,
27 3-aminopyrrolidine, N-(3-aminopropyl)-morpholine, etc.
28 Among the heterocyclic compounds, the piperazines are
29 preferred.

30
31 Typical polyamines that can be used to form the compounds of
32 this invention include the following:

33
34

28

01 ethylene diamine, 1,2-propylene diamine, 1,3-propylene
02 diamine, diethylene triamine, triethylene tetramine,
03 hexamethylene diamine, tetraethylene pentamine, methyl-
04 aminopropylene diamine, N-(betaaminoethyl)piperazine,
05 N,N'-di(betaaminoethyl)piperazine, N,N'-di(beta-amino-
06 ethyl)-imidazolidone-2, N-(beta-cyanoethyl)ethane-1,2-
07 diamine, 1,3,6,9-tetraaminooctadecane, 1,3,6-triamino-9-
08 oxadecane, N-(beta-aminoethyl)diethanolamine, N-methyl-1,2-
09 propanediamine, 2-(2-aminoethylamino)-ethanol, 2-[2-(2-amino-
10 ethylamino)ethylamino]-ethanol.

11

12 Another group of suitable polyamines are the propylene-
13 amines, (bisaminopropylethylenediamines). Propyleneamines
14 are prepared by the reaction of acrylonitrile with an
15 ethyleneamine, for example, an ethyleneamine having the
16 formula $H_2N(CH_2CH_2NH)_jH$ wherein j is an integer from 1 to 5,
17 followed by hydrogenation of the resultant intermediate.
18 Thus, the product prepared from ethylene diamine and
19 acrylonitrile would be $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$.

20

21 In many instances the polyamine used as a reactant in the
22 production of polysuccinimides of the present invention is
23 not a single compound but a mixture in which one or several
24 compounds predominate with the average composition indi-
25 cated. For example, tetraethylene pentamine prepared by the
26 polymerization of aziridine or the reaction of dichloro-
27 ethylene and ammonia will have both lower and higher amine
28 members, e.g., triethylene tetramine, substituted
29 piperazines and pentaethylene hexamine, but the composition
30 will be largely tetraethylene pentamine and the empirical
31 formula of the total amine composition will closely
32 approximate that of tetraethylene pentamine. Finally, in
33 preparing the polysuccinimide for use in this invention,
34 where the various nitrogen atoms of the polyamine are not

29

01 geometrically equivalent, several substitutional isomers are
02 possible and are encompassed within the final product.
03 Methods of preparation of polyamines and their reactions are
04 detailed in Sidgewick's "The Organic Chemistry of Nitrogen",
05 Clarendon Press, Oxford, 1966; Noller's "Chemistry of
06 Organic Compounds", Saunders, Philadelphia, 2nd Ed., 1957;
07 and Kirk-Othmer's "Encyclopedia of Chemical Technology", 2nd
08 Ed., especially Volume 2, pp. 99-116.

09

10

B(3) General Preparation

11

12 The polysuccinimides are prepared by reacting copolymer with
13 a polyamine to form a mono-, bis-polysuccinimide, higher
14 polysuccinimide or mixtures thereof. The charge mole ratio
15 of polyamine to succinic groups in copolymer may determine
16 the mixture of polysuccinimides formed. For example, a
17 product comprising mono-, bis-polysuccinimide or higher
18 polysuccinimide can be prepared by controlling the molar
19 ratios of the polyamine and succinic groups in copolymer and
20 the polyamine used. Thus, if about one mole of polyamine is
21 reacted with one mole of succinic group in the copolymer, a
22 predominately mono-polysuccinimide product will be prepared.
23 If about two moles of succinic group in the copolymer are
24 reacted per mole of polyamine, a bis-polysuccinimide may be
25 prepared. If higher amounts of succinic group in copolymer
26 are used, higher polysuccinimides may be prepared provided
27 that there are sufficient basic amino groups (or sufficient
28 branching) in the polyamine to react with a succinic group
29 from each of several copolymer molecules to produce the
30 higher polysuccinimide. Due to the cross-linking of
31 copolymer molecules by the polyamine component, compositions
32 of very high molecular weight, on the order of about 10,000
33 to about 100,000 may be prepared.

34

01 The reaction of a polyamine with an alkenyl or alkyl
02 succinic anhydride to produce the polyamino alkenyl or alkyl
03 succinimides is well known in the art and is disclosed in
04 U.S. Patents Nos. 2,992,708; 3,018,291; 3,024,237;
05 3,100,673; 3,219,666; 3,172,892; and 3,272,746. The above
06 are incorporated herein by reference for their disclosures
07 of preparing alkenyl or alkyl succinimides. The present
08 polysuccinimides may be prepared by following the general
09 procedures described therein.

10
11 Accordingly, polyamine and copolymer are contacted at the
12 desired molar ratio to give the desired mono-, bispoly-
13 succinimides or higher polysuccinimides or mixtures thereof.
14 The reaction may be carried out neat or preferably in
15 solution. Suitable solvents include organic solvents,
16 including alcohols, aliphatic and aromatic solvents, and the
17 like. The reaction is conducted at a temperature of about
18 80°C to about 250°C, preferably from about 120°C to about
19 180°C and is generally complete within about 2 to about 24
20 hours. The reaction may be conducted under ambient pressure
21 and atmospheric conditions, although a nitrogen atmosphere
22 at atmospheric pressure may be preferred. The desired
23 product may be isolated by conventional procedures, such as
24 water wash and stripping, usually with the aid of vacuum, of
25 any residual solvent.

26

27 B(4) General Preparation of Preferred Polysuccinimides

28

29 The preferred polysuccinimides of the present invention are
30 prepared by reacting a polyPIBSA copolymer of the present
31 invention with polyamine. The charge mole ratio of
32 polyamine to succinic groups in the polyPIBSA will effect
33 whether monopolysuccinimides, bis-polysuccinimides, or
34 higher polysuccinimides or mixtures thereof are produced

31

01 and/or predominate. Accordingly, with a charge mole ratio
02 (CMR) of about one mole of polyamine per mole of succinic
03 groups in the polyPIBSA primarily mono-polysuccinimide will
04 be formed. However, at a CMR of 0.5 mole polyamine per mole
05 of succinic group in the polyPIBSA, there is a tendency to
06 form bis-polysuccinimides where the polyamine component acts
07 to link two succinic groups, thusly forming a cross-linked
08 composition. Accordingly, the reaction of polyPIBSA and
09 polyamine will yield a mixture of products which I term
10 "polysuccinimides" and which term includes monopolysuccini-
11 mides, also higher succinimides and bis-polysuccinimides and
12 compositions of intermediate structure.

13
14 The reaction is carried out by contacting polyamine and
15 polyPIBSA. Although the ratio of the reactants is not
16 critical, as noted above a CMR may be chosen so as to yield
17 desired polysuccinimide proportions. The reaction is
18 carried out at a temperature sufficient to cause reaction of
19 the polyamine with a succinic group of the polyPIBSA. In
20 particular, reaction temperatures from about 120°C to about
21 180°C are preferred, with temperatures from about 140°C to
22 about 170°C being especially preferred.

23
24 The reaction may be conducted neat - that is both the
25 polyamine and the polyPIBSA are combined and then stirred at
26 the reaction temperature.

27
28 Alternatively, the reaction may be conducted in a diluent.
29 For example, the reactants may be combined in a solvent such
30 as aliphatic or aromatic solvents, and the like, and then
31 stirred at the reaction temperature. After completion of
32 the reaction, volatile components may be stripped off. When

33
34

32

01 a diluent is employed, it is preferably inert to the reac-
02 tants and products formed and is generally used in an amount
03 sufficient to ensure efficient stirring.

04

05 Preferred are polyamines having from about 2 to about 12
06 amine nitrogen atoms and from about 2 to about 40 carbon
07 atoms. The more preferred polyamines employed in this
08 reaction are generally represented by the formula:

09

10
$$\text{H}_2\text{N}(\text{YNH})_a\text{H}$$

11

12 wherein Y is an alkylene group of 2 to 10 carbon atoms,
13 preferably from 2 to 6 carbon atoms, and a is an integer
14 from about 1 to 11, preferably from 1 to 6. However, the
15 preparation of these alkylene polyamines does not produce a
16 single compound and cyclic heterocycles, such as piperazine,
17 may be included to some extent in the alkylene diamines.

18

19 B(5) Preferred Polysuccinimides

20

21 (a) Monopolysuccinimides

22

23 Preferred monopolysuccinimides include those having the
24 following formula:

25

26

27

28

29

30

31

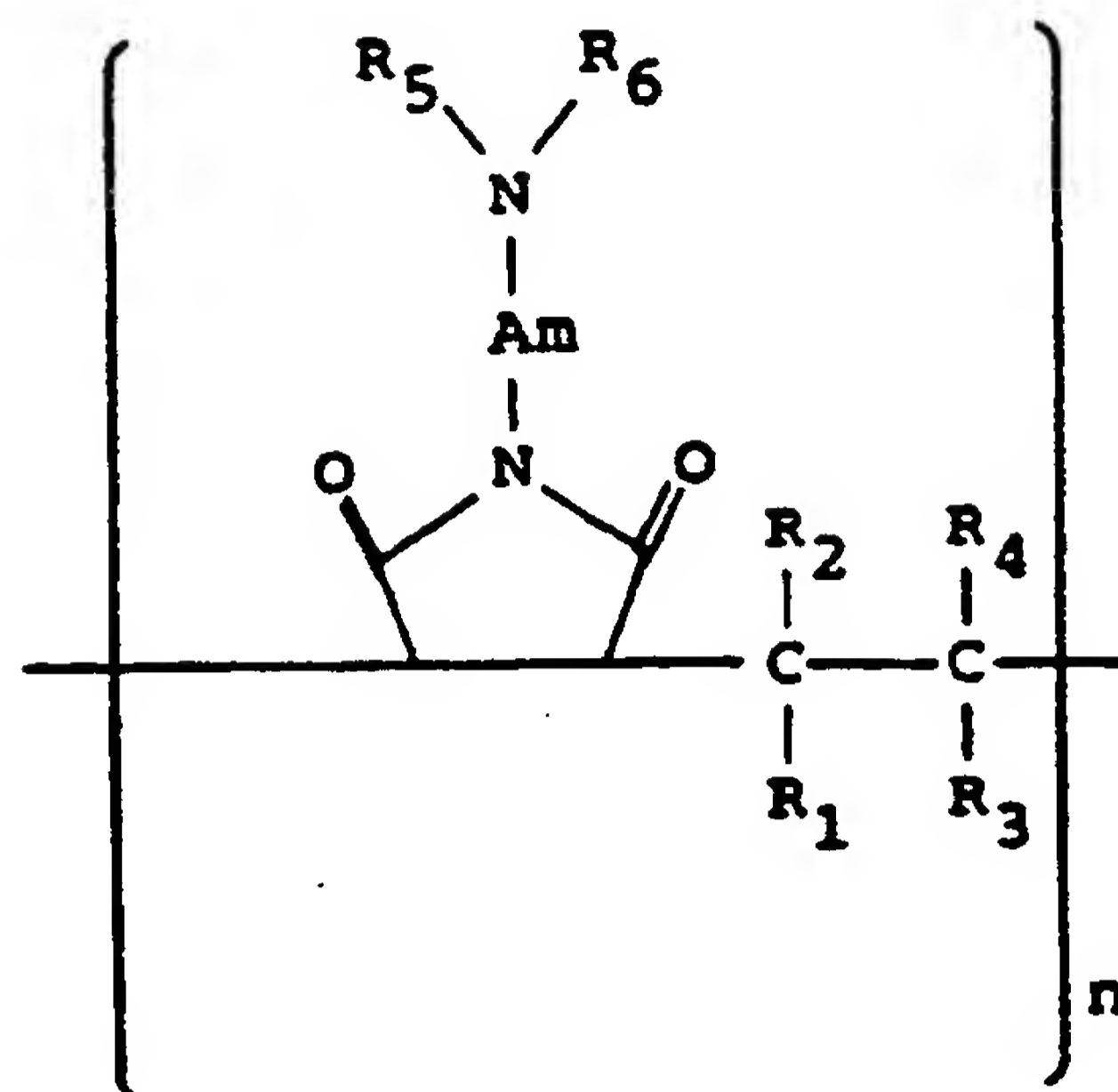
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wherein Am is a linking group having from about 0 to about 10 amine nitrogen atoms and from about 2 to about 40 carbon atoms; n is 1 or greater and R_1 , R_2 , R_3 and R_4 are selected from hydrogen lower alkyl of 1 to 6 carbon atoms; and high molecular weight polyalkyl; wherein either R_1 and R_2 are hydrogen and one of R_3 and R_4 is lower alkyl and the other is high molecular weight polyalkyl or R_3 and R_4 are hydrogen and one of R_1 and R_2 is lower alkyl and the other is high molecular weight polyalkyl; and R_5 and R_6 are independently hydrogen, lower alkyl of 1 to 6 carbon atoms, phenyl or taken together are alkylene of 3 to 6 carbon atoms to give a ring.

Preferred high molecular weight polyalkyl groups include polyisobutyl groups having at least about 30 carbon atoms, more preferably, at least about 50 carbon atoms. Especially preferred are polyisobutyl groups having an average molecular weight of about 500 to about 5000, more preferably from about 900 to about 2500.

34

- 01 Preferred lower alkyl groups include methyl and ethyl.
02 Especially preferred are compounds where the lower alkyl
03 group is methyl.
04
05 Preferred are compounds where R_5 and R_6 are hydrogen or
06 methyl; preferred R_5 and R_6 groups include hydrogen.
07
08 Preferred are Am groups having from about 0 to about 10
09 amine nitrogen atoms and from about 2 to about 40 carbon
10 atoms. More preferred are Am groups of the formula
11 $-[(ZNH)_p]Z'-$ wherein Z and Z' are independently alkylene of
12 from about 2 to about 6 carbon atoms and p is an integer
13 from 1 to 6. Especially preferred are Am groups where Z and
14 Z' are ethylene and p is 2, 3 or 4.
15
16 Preferred are compounds where n is from about 2 to about 20,
17 more preferably from about 2 to about 10.
18
19 Preferred are compounds having an average degree of polymer-
20 ization of from about 1.1 to about 20, more preferably from
21 about 1.5 to about 10.

22
23 (b) Bis-polysuccinimides

- 24
25 Preferred polysuccinimides include those which partially
26 comprise at least in part a bis-polysuccinimide structure.
27 Some of these preferred polysuccinimides are random poly-
28 succinimides which comprise units selected from:
29
30
31
32
33
34

35

01

02

03

04

05

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07

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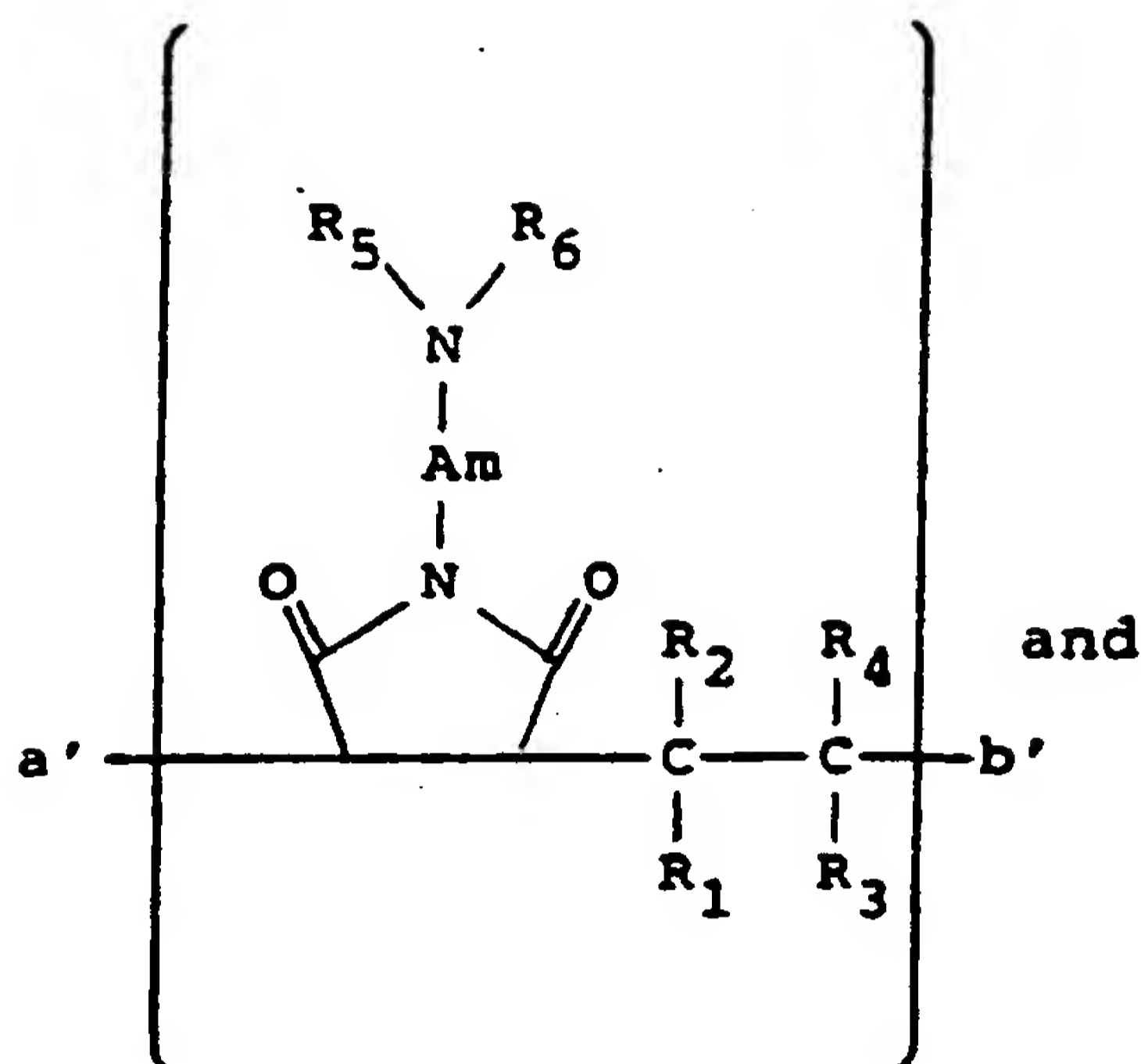
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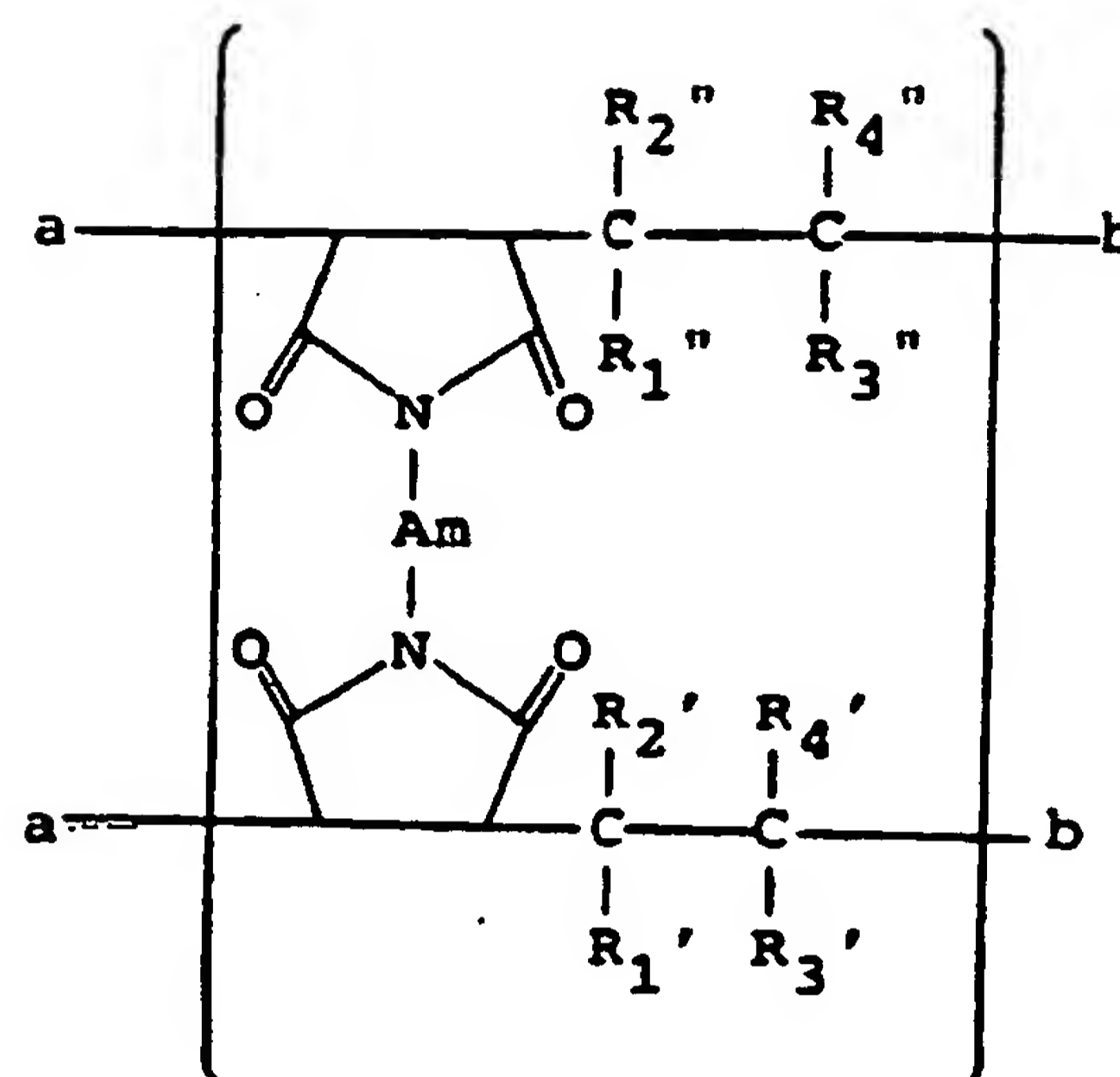
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A



and

B



wherein Am is a linking group having from about 0 to 10 amine nitrogen atoms and from about 2 to 40 carbon atoms; R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , R_4' , R_1'' , R_2'' , R_3'' , and R_4'' are selected from hydrogen, lower alkyl of one to 6 carbon atoms and high molecular weight polyalkyl; wherein either R_1 and R_2 are hydrogen and one of R_3 and R_4 is lower alkyl and the other is polyalkyl, or R_3 and R_4 are hydrogen and one of R_1 and R_2 is lower alkyl and the other is polyalkyl; either R_1' and R_2' are hydrogen and one of R_3' and R_4' is lower alkyl and the other is polyalkyl, or R_3' and R_4' are hydrogen and one of R_1' and R_2' is lower alkyl and the other is polyalkyl; and either R_1'' and R_2'' are hydrogen and one of R_3'' and R_4'' is lower alkyl and the other is polyalkyl or R_3'' and R_4'' are hydrogen and one of R_1'' and R_2'' is lower alkyl and the other is polyalkyl and R_5 and R_6 are independently hydrogen, lower alkyl of 1 to 6 carbon atoms, phenyl or taken together are alkylene of 3 to 6 carbon atoms to give a ring; a, a', b and b' are sites for a covalent bond provided that at least one a or a' site of each unit is covalently bonded to a b or b' site.

01 Preferred polyalkyl groups include polyisobutyl groups
02 having at least about 30 carbon atoms, more preferably at
03 least about 50 carbon atoms. Especially preferred are
04 polyisobutyl groups having an average molecular weight of
05 about 500 to about 5000, more preferably from about 900 to
06 about 2500.

07
08 Preferred lower alkyl groups include methyl and ethyl;
09 especially preferred is ethyl.

10
11 Preferred Am groups include those having the formula
12 $\{(ZNH)pZ'\}$ — wherein Z and Z' are independently alkylene of 2
13 to 6 carbon atoms and p is an integer from 0 to 5.
14 Especially preferred are Am groups wherein Z and Z' are
15 ethylene and p is 1, 2 or 3.

16
17 Preferred are random polysuccinimides where the average sum
18 of A and B units is from about 2 to about 50. preferred are
19 random polysuccinimides having molecular weights of from
20 about 10,000 to about 150,000.

21
22 Preferred are compounds in which the bis-succinimide
23 structure predominates, that is those having more B units
24 than A units, preferably on the order of about 2 to about 10
25 times as many B units as A units. Such compounds are
26 preferred in part due to their high average molecular
27 weights, on the order of about 10,000 to about 150,000 which
28 may be related to their exhibiting an advantageous V.I.
29 credit as well as dispersantability when used in a
30 lubricating oil composition.

31
32 It is believed that polysuccinimide compounds in which a
33 significant portion comprises a bis-polysuccinimide
34 structure (an embodiment which is exemplified in FIG. 1)

01 comprise network or ladder polymers. Such polymers are
02 cross-linked in an orderly manner. It is believed that this
03 orderly cross-linking allows for the formation of composi-
04 tions having very high molecular weights, on the order of
05 about 10,000 to about 150,000 and also contributes to the
06 advantageous properties of these compositions including
07 improved dispersancy and V.I. credit. In addition, due to
08 the cross-linking of the copolymer molecules by the poly-
09 amine to form the polysuccinimides of the above-noted
10 structure, such products are harder to hydrolyze and are
11 more stable to shear forces than are those polysuccinimides
12 which do not form the ladder structure.

13

14

(c) Higher Polysuccinimides

15

16 Higher polysuccinimides are prepared by reacting the copoly-
17 mers of the present invention with a polyamine having
18 branching such that it can react with a succinic group from
19 each of greater than two copolymer molecules. Due to this
20 crosslinking, it is believed that these higher polysucci-
21 nimides may have gel-like properties besides the dispersant
22 properties possessed by the other polysuccinimides.

23

24

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C. POLYAMINO POLYSUCCINIMIDES WHEREIN ONE
OR MORE OF THE NITROGENS IS SUBSTITUTED
WITH HYDROCARBYL OXYCARBONYL, HYDROXY HYDROCARBYL
OXYCARBONYL, OR HYDROXY POLY(OXYALKYLENE)OXYCARBONYL)
OR THE POLYSUCCINIMIDE IS OTHERWISE POST-TREATED

28 Commonly-assigned U.S. Patent No. 4,612,132 discloses poly-
29 amino alkenyl or alkyl succinimides wherein one or more of
30 the nitrogens of the polyamino moiety is substituted with a
31 hydrocarbyl oxycarbonyl, or a hydroxy hydrocarbyl oxycar-
32 bonyl wherein said hydrocarbyl contains from 1 to about 20
33 carbon atoms and said hydroxy hydrocarbyl contains from
34 about 2 to about 20 carbon atoms which may be prepared by

38

01 reaction with a cyclic carbonate; by reaction with a linear
02 mono- or polycarbonate; or by reaction with a suitable
03 chloroformate and hydroxy poly(oxyalkylene)oxycarbonyl which
04 may be formed by reaction with a suitable chloroformate.

05 U.S. Patent No. 4,612,132 also discloses processes for the
06 preparation of such modified polyamino alkenyl or alkyl
07 succinimides.

08

09 U.S. Patent No. 4,612,132 also discloses the post-treating
10 of hydroxyhydrocarbyl carbamates prepared from polyamino
11 alkenyl or alkyl succinimides with an alkenyl or alkyl
12 succinic anhydride.

13

14 In addition, U.S. Patent No. 4,612,132 discloses the reac-
15 tion of the modified succinimides disclosed therein with
16 boric acid or similar boron compound to give borated
17 dispersants. Accordingly, the disclosure of U.S. Patent
18 No. 4,612,132 is incorporated herein by reference.

19

20 Commonly assigned U.S. Patent No. 4,585,566 discloses
21 improved dispersants prepared by reacting other
22 nitrogen-containing dispersants with cyclic carbonates, the
23 disclosure of which is incorporated herein by reference.

24

25 Accordingly, by following the procedures disclosed in U.S.
26 Patents Nos. 4,612,132 and 4,585,566, modified polysuccini-
27 mides may be prepared. Thus, the polyamino polysuccinimides
28 wherein one or more of the nitrogens of the polyamino moiety
29 is substituted with a hydrocarbyl oxycarbonyl, or a hydroxy
30 hydrocarbyl oxycarbonyl wherein said hydrocarbyl contains
31 from 1 to about 20 carbon atoms and said hydroxy hydrocarbyl
32 contains from 2 to about 20 carbon atoms may be prepared by
33 reaction with a cyclic carbonate; by reaction with a linear
34 mono- or poly-carbonate; or by reaction with a suitable

37

01 chloroformate. Hydroxy poly(oxyalkylene) oxycarbonyl may be
02 formed by reaction with a suitable chloroformate. Also,
03 hydroxy hydrocarbyl carbamates prepared from the polysuccinimides of the present invention may be post-treated with an
04 alkenyl or alkyl succinic anhydride [or even the copolymers
05 of the present invention (such as polyPIBSA) according to
06 the procedures disclosed in U.S. Patents Nos. 4,612,132 and
07 4,585,566. The products so produced are effective disper-
08 sant and detergent additives for lubricating oils and for
09 fuel.
10

11
12 The polysuccinimides and modified polysuccinimides of this
13 invention can also be reacted with boric acid or a similar
14 boron compound to form borated dispersants having utility
15 within the scope of this invention. In addition to boric
16 acid (boron acid), examples of suitable boron compounds
17 include boron oxides, boron halides and esters of boric
18 acid. Generally from about 0.1 equivalents to 10 equiva-
19 lents of boron compound to the polysuccinimide or modified
20 polysuccinimide may be employed.

21
22 Commonly-assigned U.S. Patent No. 4,615,826 discloses the
23 treating of a succinimide having at least one basic nitrogen
24 with a fluorophosphoric acid or ammonium salt thereof to
25 give a hydrocarbon-soluble fluorophosphoric acid adduct..
26 Accordingly, the disclosure of U.S. Patent No. 4,615,826 is
27 incorporated herein by reference.

28
29 By following the disclosure of U.S. Patent No. 4,615,826,
30 hydrocarbon-soluble fluorophosphoric adducts of the poly-
31 succinimides of the present invention may be prepared. Such
32 adducts comprise the reaction product of a polysuccinimide
33 of the present invention and a fluorophosphoric acid or
34

40

01 ammonium salt thereof wherein the amount of said fluoro-
02 phosphoric acid or salt thereof is from about 0.1 to about 1
03 equivalent per equivalent of basic nitrogen atom.

04

05 The copolymers of the present invention, including preferred
06 copolymers such as polyPIBSA may be post-treated with a wide
07 variety of other post-treating reagents. U.S. Patent
08 No. 4,234,435, the disclosure of which is incorporated
09 herein by reference, discloses reacting succinic acylating
10 agents with a variety of reagents to give post-treated
11 carboxylic acid derivative compositions which are useful in
12 lubricating oil compositions.

13

14

D. LUBRICATING OIL COMPOSITIONS

15

16 The copolymers, polysuccinimides and modified polysuccini-
17 mides of this invention are useful as detergent and disper-
18 sant additives when employed in lubricating oils. When
19 employed in this manner, the additives of the present
20 invention are usually present in from 0.2 to 10 percent by
21 weight to the total composition and preferably at about 0.5
22 to 8 percent by weight and more preferably at about 1 to
23 about 6 percent by weight. The lubricating oil used with
24 the additive compositions of this invention may be mineral
25 oil or synthetic oils of lubricating viscosity and prefer-
26 ably suitable for use in the crankcase of an internal
27 combustion engine. Crankcase lubricating oils ordinarily
28 have a viscosity of about 1300 CSt 0°F to 22.7 CSt at 210°F
29 (99°C). The lubricating oils may be derived from synthetic
30 or natural sources. Mineral oil for use as the base oil in
31 this invention includes paraffinic, naphthenic and other
32 oils that are ordinarily used in lubricating oil composi-
33 tions. Synthetic oils include both hydrocarbon synthetic
34 oils and synthetic esters. Useful synthetic hydrocarbon

41

01 oils include liquid polymers of alpha olefins having the
02 proper viscosity. Especially useful are the hydrogenated
03 liquid oligomers of C₆ to C₁₂ alpha olefins such as 1-decene
04 trimer. Likewise, alkyl benzenes of proper viscosity, such
05 as didodecyl benzene, can be used.

06

07 Blends of hydrocarbon oils with synthetic oils are also
08 useful. For example, blends of 10 to 25 weight percent
09 hydrogenated 1-decene trimer with 75 to 90 weight percent
10 150 SUS (100°F) mineral oil gives an excellent lubricating
11 oil base.

12

13 Lubricating oil concentrates are also included within the
14 scope of this invention. The concentrates of this invention
15 usually include from about 90 to 10 weight percent, prefer-
16 ably from about 90 to about 50 weight percent, of an oil of
17 lubricating viscosity and from about 10 to 90 weight per-
18 cent, preferably from about 10 to about 50 weight percent,
19 of an additive of this invention. Typically, the concen-
20 trates contain sufficient diluent to make them easy to
21 handle during shipping and storage. Suitable diluents for
22 the concentrates include any inert diluent, preferably an
23 oil of lubricating viscosity, so that the concentrate may be
24 readily mixed with lubricating oils to prepare lubricating
25 oil compositions. Suitable lubricating oils which can be
26 used as diluents typically have viscosities in the range
27 from about 35 to about 500 Saybolt Universal Seconds (SUS)
28 at 100°F (38°C), although an oil of lubricating viscosity
29 may be used.

30

31 Other additives which may be present in the formulation
32 include rust inhibitors, foam inhibitors, corrosion
33 inhibitors, metal deactivators, pour point depressants,
34 antioxidants, and a variety of other well-known additives.

42

01 It is also contemplated the additives of this invention may
02 be employed as dispersants and detergents in hydraulic
03 fluids, marine crankcase lubricants and the like. When so
04 employed, the additive is added at from about 0.1 to 10
05 percent by weight to the oil. Preferably, at from 0.5 to 8
06 weight percent.

07

08

E. FUEL COMPOSITIONS

09

10 When used in fuels, the proper concentration of the additive
11 necessary in order to achieve the desired detergency is
12 dependent upon a variety of factors including the type of
13 fuel used, the presence of other detergents or dispersants
14 or other additives, etc. Generally, however, and in the
15 preferred embodiment, the range of concentration of the
16 additive in the base fuel is 10 to 10,000 weight parts per
17 million, preferably from 30 to 5000 parts per million of the
18 additive per part of base fuel. If other detergents are
19 present, a lesser amount of the additive may be used.
20 The additives of this invention may be formulated as a fuel
21 concentrate, using an inert stable oleophilic organic
22 solvent boiling in the range of about 150° to 400°F.
23 Preferably, an aliphatic or an aromatic hydrocarbon solvent
24 is used, such a benzene, toluene, xylene or higher-boiling
25 aromatics or aromatic thinners. Aliphatic alcohols of about
26 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol,
27 n-butanol and the like, in combination with hydrocarbon
28 solvents are also suitable for use with the fuel additive.
29 In the fuel concentrate, the amount of the additive will be
30 ordinarily at least 5 percent by weight and generally not
31 exceed 70 percent by weight, preferably from 5 to 50 and
32 more preferably from 10 to 25 weight percent.

33

34

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01 The following examples are offered to specifically
02 illustrate this invention. These examples and illustrations
03 are not to be construed in any way limiting the scope of
04 this invention.

05

06

EXAMPLES

07

Example 1

08

09

Preparation of Polyisobutyl-24 PolyPIBSA

10

11 To a 12-liter, 3-neck flask equipped with an overhead
12 stirrer, thermometer, condenser, and heating mantle under
13 nitrogen atmosphere was added 5,000 grams (5.265 mole) of
14 polyisobutene of about 950 molecular weight having the trade-
15 name ULTRAVIS-10 obtained from BP Chemicals wherein the
16 methylvinylidene isomer comprised about 70% of the total
17 composition, 1547.1 grams (15.79 mole) maleic anhydride, and
18 2,500 ml chloroform. The mixture was heated to reflux, and
19 to this was added 67.21 grams (0.41 mole) 22'-azobis
20 (2-methyl-propionitrite) ("AIBN"). The mixture was refluxed
21 for two hours at which time an additional 67.21 grams of
22 AIBN was added. This was followed by another two hours of
23 reflux and a third charge (66.58 grams) of AIBN. A total of
24 201 grams (1.2 mole) of AIBN was added. The reaction
25 mixture was refluxed a total of 20 hours, and then allowed
26 to cool. Two layers formed. The lower phase which
27 contained mostly chloroform and unreacted maleic anhydride
28 was discarded. The upper layer which contained mainly
29 product and unreacted polyisobutene was separated. Solvent
30 and maleic anhydride were removed in vacuo. A total of
31 4,360 grams of product having a saponification number of
32 40.4 was recovered.

33

34

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01

Example 2

02

Preparation of Polyisobutyl-24 PolyPIBSA

03

04 To a 1-liter 3-neck flask equipped with a thermometer,
05 overhead stirrer, nitrogen inlet and water condenser, was
06 added 165.02 grams (0.174 mole) polyisobutylene (ULTRAVIS-10
07 from BP Chemicals) and 105 ml dichloroethane, then
08 16.4 grams (0.167 mole) maleic anhydride were added. The
09 resulting mixture was heated to about 45°C, and 3.3 grams
10 (0.017 mole) tert-butylperbenzoate was added. The resulting
11 mixture was heated to reflux (83°C). The reaction mixture
12 was heated (with stirring) for a total of 30 hours. The
13 reaction mixture was allowed to cool. The solvent was
14 removed in vacuo. Unreacted maleic anhydride was removed by
15 heating the residue to 150°C at 0.1 mm Hg vacuum. A total
16 of 176.0 grams product was obtained, which had an average
17 molecular weight of about 5000. The conversion was about
18 60%. The saponification number was 73.3.

19

20

Examples 3 to 15 and Comparison Examples 1C to 5C

21

22 Table I tabulates additional preparations following the
23 basic synthetic procedure outlined in Examples 1 and 2.
24 Table I lists the reactants, reaction temperature, time and
25 solvent, and free radical initiator used.

26

27 Example 12 was prepared using polyisobutene of about 1300
28 molecular weight having the trade name ULTRAVIS-30 obtained
29 from BP chemicals wherein the methylvinylidene isomer
30 comprised about 70% of the total composition.

31

32 Comparison Examples 1C to 5C were prepared using a
33 polyisobutylene of about 950 molecular weight prepared with

34

45

01 AlCl₃ catalysis having the trade name Parapol 950 obtained
 02 from Exxon Chemical.

TABLE I

07	Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator* (g)	Temp °C	Time Hrs.
10	2	Ultravis-10 (165.09)	16.4	Dichloroethane (105)	TBPB (3.3)	83	30
12	3	Ultravis-10 (384.6)	119	Toluene (250)	AIBN (15.5)	110	6
14	4	Ultravis-10 (330)	32.3	Chlorobenzene (210)	DTBP (5.8)	138	30
16	5	Ultravis-10 (5000)	1547	Dichloroethane (2500)	AIBN (200)	83	13
18	6	Ultravis-10 (384.6)	119	Chloroform (250)	AIBN (15.5)	74	24
20	7	Ultravis-10 (384.6)	119	Methylene Chloride (250)	AIBN (15.5)	40	94
22	8	Ultravis-10 (330)	32.3	Toluene (210)	DTBP (5.8)	110	30
24	9	Ultravis-10 (330)	32.3	Xylene (210)	DTBP (5.8)	144	39
26	10	Ultravis-10 (330)	32.3	Xylene (210)	DTBP (5.8)	114	4
28	11	Ultravis-10 (330)	32.3	Toluene (210)	DTBP (5.8)	110	4
31	12	Ultravis-30 (217.1)	16.4	Dichloroethane (105)	TBPB (3.3)	83-184	26
33	13	Ultravis-10 (3350)	328.3	Chlorobenzene (1600)	DTBP (42.6)	138	28

46

TABLE I (Cont'd)

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator* (g)	Temp °C	Time Hrs.
14	Ultravis-10 (5000)	515.8	Chloroform (3000)	TBPB (102.8)	72	54
15	Ultravis-10 (10,000)	1031	Chloroform (6000)	TBPB (205.6)	72 then 140	48 2
1C	Parapol 950 (384.6)	119	Toluene (250)	AIBN (15.5)	110	6
2C	Parapol 950 (76.4)	23.8	Dichloroethane (50)	AIBN (2.33)	83	4
3C	Parapol 950 (330)	32.3	Toluene (210)	DTBP (5.8)	110	30
4C	Parapol 950 (330)	32.3	Xylene (210)	DTBP (5.8)	114	30
5C	Parapol 950 (330)	32.3	Chlorobenzene (210)	DTBP (5.8)	138	30

* AIBN = 2,2'-azobis (2-methyl-propionitrile); DTBP = di-tert-butyl peroxide; TBPB = tert-butyl peroxybenzoate

** Molecular weight 1300

Example 16

A 500-ml, 3-necked flask was charged with 100g of a polyPIBSA polybutene mixture (prepared according to the method of Example 5) which comprised about 38 weight percent polyPIBSA and about 62 weight percent unreacted polyisobutene (of which about 68 weight percent comprised the methylvinylidene isomer). The mixture was heated to 70°C. Then, 8g maleic anhydride and 1.7g di-tert-butyl peroxide were added to the mixture. The mixture was stirred and

47

01 heated to 150°C for 5 hours. After allowing the mixture to
02 cool, 150 ml hexane was added to precipitate unreacted
03 maleic anhydride which was then removed by filtration. The
04 hexane was removed by stripping for 4 hours at 36 mm Hg
05 (abs) at 90°C. The product had a maleic anhydride content
06 of 0.08 weight percent.

07

08

Example 17A

09

10 A 22-liter, 3-necked flask was charged with 3752g of
11 polyisobutene (BP Ultravis 10) and 2800g of a polyPIBSA
12 polyisobutene mixture (prepared according to Example 13)
13 which comprised about 57 weight percent polyPIBSA and about
14 43 weight percent unreacted polyisobutene). The mixture was
15 heated to 91°C; then 14g maleic anhydride and 2.7g
16 di-tert-butyl peroxide (DTBP) were added. A slight exotherm
17 was noticed where the temperature increased to 147°C. The
18 mixture was stirred and heated at 140°C for one hour. After
19 standing at room temperature overnight, the mixture was
20 heated to 140°C and 378g maleic anhydride and 56.7g of DTBP
21 were added. The mixture was stirred and heated at 140°C for
22 6.5 hours. The mixture was allowed to cool to ambient
23 temperature overnight. The mixture was heated to 80°C and
24 vacuum was applied at 28 inches Hg (vac); the temperature
25 was increased to 200°C. The mixture was stripped at 200°C
26 and 28 inches Hg (vac) for 2 hours to remove unreacted
27 maleic anhydride.

28

29

Example 17B

30

31 A 22-liter, 3-necked flask was charged with 8040g
32 polyisobutene (BP Ultravis 10) and 6000g of a
33 polyPIBSA/polybutene mixture prepared according to
34 Example 17A. The mixture was heated to 109°C, then 840g

48

01 maleic anhydride and 126g DTBP were added. The resulting
02 mixture was stirred and heated at 140°C for 5.25 hours. The
03 mixture was cooled to ambient temperature. The mixture was
04 then heated to 128°C with stirring and an additional 153g
05 maleic anhydride and 23g DTBP were added. The mixture was
06 stirred and heated at 140°C for 3.5 hours and then an
07 additional 153g maleic anhydride and 11.8g DTBP were added.
08 The mixture was stirred and heated at 140°C for an
09 additional 3.67 hours. The mixture was cooled to ambient
10 temperature. The mixture was then stirred and heated at
11 186°C for one hour while vacuum was applied to strip the
12 unreacted maleic anhydride from the product. The product
13 had a saponification number of 85.8 mg KOH/g.

14

15

Example 18

16

17

Preparation of PolyPIBSA TETA

18

Polysuccinimide with a High Degree of Polymerization

19

20 To a 12-liter flask equipped with a Dean Stark trap,
21 overhead stirrer and heating mantle under nitrogen was added
22 4340 g polyPIBSA prepared according to Example 1
23 (saponification No. 40.4 mg KOH/g, molecular weight about
24 9000). The resulting mixture was heated to 130°C with
25 stirring, then 163.7g (1.12 mole) triethylenetetraamine
26 (TETA) were added. The reaction mixture was stirred
27 overnight at 160°C to 215°C; 24 ml water were collected (in
28 the Dean Stark trap) The reaction mixture was allowed to
29 cool.

30

31 Obtained was 4360 g of a polysuccinimide of about 58,000
32 molecular weight having the following characteristics:
33 1.45%N, TAN 1.01, TBN 26.9, viscosity at 100°C 2649 cSt.
34 The molecular weight was determined using 1-1000Å and 1-500Å

49

01 ultrastyrogel columns connected in series using 10%
02 propylamine 90% THF as a solvent and comparing the retention
03 time with known (molecular weight) polystyrene standards.
04

05 Example 19

06
07 Preparation PolyPIBSA TEPA
08 Polysuccinimide With a High Degree of Polymerization

09 To a 3-neck one-liter flask equipped with heating mantle,
10 overhead stirrer and Dean Stark trap, was added 213.4 g
11 polyPIBSA prepared according to the method of Example 5
12 (molecular weight about 6000). The system was heated to
13 90°C with stirring; then 18.98 g of tetraethylene pentaamine
14 (TEPA) (0.1003 g). The resulting mixture was heated to
15 176°C under nitrogen sweep. A small amount of water (about
16 0.5 ml) was removed. After 3.5 hours, the mixture was
17 placed under vacuum and was heated under vacuum for 0.5
18 hours; the heating was then stopped. Obtained was 226.9 g
19 of product, a polyPIBSA TEPA polysuccinimide.
20

21 Example 20

22
23 Preparation of PolyPIBSA TETA
24 Polysuccinimide With a High Degree of Polymerization

25 To a 12-liter flask equipped with an overhead stirrer,
26 heating mantle and Dean Stark trap, under nitrogen sweep,
27 was added 4539 g polyPIBSA prepared according to Example 5
28 (saponification number 36.3, molecular weight about 6600).
29 The system was heated to 125°C with stirring; then 131.6 g
30 triethylene tetraamine (TETA) was added. The reaction
31 mixture was heated to 165°C for 5 hours. A total of 21.5 ml
32 water was collected in the Dean Stark trap. The mixture was
33 then heated under vacuum at 180°C for two hours. The
34 reaction mixture was allowed to cool. Obtained was 4589 g

50

01 of product, a polysuccinimide of about 35,000 molecular
02 weight having the following characteristics: %N 1.14, TAN
03 2.33, TBN 20.1, viscosity at 100°C 1817 cSt.

04

05

Example 21

06

07

08

Preparation of PolyPIBSA TETA
Polysuccinimide with a Low Degree of Polymerization

09 To a 5-liter flask equipped with a heating mantle, overhead
10 stirrer and Dean Stark trap under nitrogen sweep, was added
11 1000 g polyPIBSA prepared according to Example 17B
12 (saponification number 85.8, molecular weight about 2500)
13 and 999 g Chevron 100NR diluent oil. The mixture was heated
14 to 60°C; then 75.78 g TETA was added. The mixture was
15 heated to 160°C and kept at temperature for 4 hours. A
16 total of 7.0 ml water was recovered from the Dean Stark
17 trap. The reaction mixture was then maintained at 160°C
18 under vacuum for 2 hours. The reaction mixture was allowed
19 to cool. Obtained was 2018.2 g of product having %N=1.35.

20

21

Example 22

22

23

24

Preparation of PolyPIBSA HPA
Polysuccinimide With a Low Degree of Polymerization

25 To a 5-liter flask equipped with a heating mantle, overhead
26 stirrer and Dean Stark trap (under nitrogen sweep) was added
27 1000 g polyPIBSA prepared according to Example 17B
28 (saponification number 85.8 molecular weight 2500) and 932
29 Chevron 100NR diluent oil. The mixture was heated to 60°C;
30 to this was added 142.45 g heavy polyamine ("HPA") No. X
31 obtained from Union Carbide Corporation. The mixture became
32 very thick. The reaction mixture was heated to 165°C and
33 maintained at that temperature for 4 hours; the mixture
34 became less viscous. Then the reaction mixture was heated

57

01 at 165°C under vacuum for 2 hours. The mixture was allowed
02 to cool. Obtained was the above-identified product having
03 %N=2.23.

04

05

Example A

06

07

Determination of Saponification Number

08

09 Saponification number was determined by using ASTM procedure
10 D94-80.

11

12 Results for the products of Examples 2 to 15 and 1C to 5C
13 are given in Table II.

14

15

Example B

16

17

Determination of Percent

18

Unreacted Polyisobutylene and Percent Product

19

20 The percent of unreacted polyisobutylene and percent product
21 were determined according to the following procedure.

22

23 A 5.0-gram sample of product was dissolved in hexane, placed
24 in a column of 80.0-gram silica gel (Davisil 62,140Å pore
25 size silica gel), and eluted with 600 ml hexane. The
26 percent unreacted polybutylene was determined by removing
27 the hexane solvent in vacuo (from the eluent) and weighing
28 the residue. The silica gel from the column was removed and
29 suspended in a 1-liter beaker with 250 ml dioxane. The
30 mixture was heated to boiling, and the filtered. The
31 process was repeated three more times. The dioxane
32 solutions were combined and then stripped to dryness in
33 vacuo and the percent product determined by weighing the
34 residue.

52

01 Results for the Products of Examples 2 to 15 and 1C to 5C
02 are tabulated in Table II.

03

04

Example C

05

06

07

Determination of Molecular Weight of
The PolyPIBSA Product and Degree of Polymerization

08

09 The molecular weight of the product was determined according
10 to the following procedure.

11

12 A 0.5% solution of product in tetrahydrofuran was injected
13 onto two 500-Å gel permeation columns (ultrastrogel)
14 connected in series. The solvent used was 1 to 3 percent
15 methanol in tetrahydrofuran. (The columns were eluted with
16 a 1% or 3 percent solutions methanol in tetrahydrofuran.)
17 Molecular weight was determined by comparison of retention
18 times of the product to the retention times of polystyrene
19 standards.

20

21 Degree of polymerization was calculated by dividing the
22 molecular weight by 1,050 (the calculated average molecular
23 weight of a monomer having one succinic group and one
24 polyisobutylene group of average molecular weight of 952).

25

26 Results for the products of Examples 2 to 15 and 1C to 5C
27 are tabulated in Table II.

28

29

Example D

30

Calculation of "PIBSA Number"

31

32 The PIBSA number was calculated by dividing the
33 saponification number by the percent product. This gave the
34 "PIBSA number" which is a saponification number for

01 polyPIBSA on a 100% actives basis. This value is tabulated
02 in Table III.

03

04 Calculated PIBSA numbers for the products of Examples 2 to
05 15 and 1C and 5C are tabulated in Table III.

06

07 It is believed that polyPIBSA comprises a copolymer having
08 alternating succinic and polyisobutyl groups.

09

10 Example E

11

12 Fourier Transform Infrared Spectra of PolyPIBSA

13

14 The Fourier Transform Infrared (FTIR) Spectra (having a
15 resolution of 2 cm^{-1}) of some of the polyPIBSA copolymers of
16 the present invention and also some comparison compounds
17 were recorded on a Nicolet MX-1 FTIR. Samples whose spectra
18 was to be run were prepared by dissolving in Chevron 100NR
19 mineral oil at a concentration of 5 percent by weight. The
20 FTIR frequency for the anhydride stretch for each sample was
21 measured and is recorded in Table IV.

22

23 As may be seen from Table IV, PIBSA prepared by the thermal
24 process ("thermal PIBSA") prepared from (a) BP ultravis
25 polyisobutene (having about 70% of the total composition in
26 the methylvinylidene configuration) and (b) Exxon Parapol
27 polyisobutene both exhibited the anhydride stretch
28 frequency at 1793 cm^{-1} . PIBSA prepared according to the
29 chlorination process ("Chlorination PIBSA") from the Exxon
30 Parapol polyisobutene had an anhydride stretch frequency at
31 1785 cm^{-1} . In contrast, copolymers of the present invention
32 comprising polyPIBSA (prepared according to Examples 3 to
33 12) exhibited anhydride stretch frequencies in the range of
34 $1777\text{ to }1783\text{ cm}^{-1}$. Comparison Examples 1C to 5C which were

54

01 prepared by reacting the Exxon Parapol polyisobutene (which
02 did not comprise at least about 20 percent of the alkyl-
03 vinylidene isomer) under free radical conditions exhibited
04 anhydride stretch absorbences in the range of 1785 to 1790
05 cm^{-1} the range for the conventional PIBSA materials. It is
06 believed that these differences are due to the 2,3-disubsti-
07 tution that is present in the one-to-one alternating
08 copolymers of the present invention.

09

10

Example F

11

Fourier Transform Infrared Spectra of Polysuccinimides

12

13
14 The Fourier Transform Infrared (FTIR) spectra of some of the
15 polysuccinimides of the present invention and also of some
16 comparison compounds were recorded. Samples were prepared
17 as described in Example E and the FTIR frequency for the
18 succinimide stretch for each sample is recorded in Table V.

19

20 As may be seen from Table V, MS-Th, monosuccinimide prepared
21 from Thermal PIBSA and BS-Th, bis-succinimide prepared from
22 Thermal PIBSA exhibit the succinimide stretch at 1705.1 cm^{-1}
23 and 1707.0 cm^{-1} , respectively. MS-Cl monosuccinimide
24 prepared from chlorination PIBSA, PS-Cl, a polysuccinimide
25 prepared from chlorination PIBSA and CS-CL, a commercial
26 succinimide prepared from chlorination PIBSA, exhibit
27 succinimide stretches at 1706.2 cm^{-1} , 1705.1 cm^{-1} and
28 1705.1 cm^{-1} , respectively.

29

30 In contrast, the polysuccinimides of the present invention
31 exhibit succinimide stretches between about 1697 cm^{-1} and
32 about 1703 cm^{-1} . It is believed that the characteristic
33 frequency for the succinimide stretch is due to the
34 disubstitution at the 2- and 3-positions in the

55

01 polysuccinimide structure, similar to the characteristic
 02 anhydride stretch exhibited by the polyPIBSA copolymers.

03

04

Example G

05

Sequence VE Test - Sludge

06

07 Formulated oils containing a polysuccinimide of the present
 08 invention prepared according to Example 18 were tested
 09 according to the Sequence VE Engine Test Procedure (Sequence
 10 VE Test Procedure, Seventh Draft, May 19, 1988) and evalu-
 11 ated for sludge. The test formulations were compared with
 12 two industry reference oils: Reference A, a poor performing
 13 oil, and Reference B, a good performing oil. Sludge ratings
 14 of 9 or greater are advantageous and generally considered
 15 passing. Results are tabulated in Table VI.

16

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TABLE II

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Product of Example	Weight Product, g	Saponifica- tion Value, mgKOH/g Sample	% Unreacted Polybutene	% Product	Molecular Wt. Product	Average Degree of Poly- meriza- tion
2	176	73.3	40	60	5,000	4.8
3	370	N/A	59	39	1,700	1.6
4	355	78.9	36	58	1,350	1.3
5	4,589+	36.3	64	36	6,600	6.3
6	374+	45.4	62	37	9,100	8.7
7	365+	43.3	57	43	11,000	10.5
8	357	78.3	36	60	1,400	1.3
9	364	78.4	40	53	1,200	1.1
10	361	79.8	39	58	1,300	1.2
11	341	35.8	65	32	1,900	1.8
12	232	39.6	35	65	8,000	5.7
13	3,605	80.3	35	57	1,350	1.3

56

01 TABLE II (Cont'd)

02			Saponifica-				Average
03			tion				Degree
04	Product	Weight	Value,	%	%	Molecular	of
05	of	Product,	mgKOH/g	Unreacted	Product	Wt.	Poly-
06	Example	g	Sample	Polybutene		Product	meriza-
07	14	5,465	N/A	33	65	3,300	3.1
08	15	10,462	N/A	35	63	12,000	11.4
09	1C	352	24.3	87	11	900	0.9
10	2C	68+	N/A	N/A	N/A	N/A	N/A
11	3C	351	87.3	52	34	900	0.9
12	4C	357	80.9	57	34	950	0.9
13	5C	356	N/A	56	32	950	0.9

15 N/A - Not Available

16 + Formed two phases - from upper phase only

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TABLE III

	<u>Product of Example</u>	<u>PIBSA Number of 100% Active Material*</u>	<u>Average Molecular Weight</u>
01			
02			
03			
04			
05			
06	2	122	5,000
07	3	N/A	1,700
08	4	136	1,350
09	5	101	6,600
10	6	123	9,100
11	7	101	11,000
12	8	131	1,400
13	9	148	1,200
14	10	138	1,300
15	11	112	1,900
16	12	61	8,000
17	13	141	1,350
18	14	N/A	3,300
19	15	N/A	12,000
20			
21	1C	219	900
22	2C	N/A	N/A
23	3C	287	900
24	4C	266	950
25	5C	295	950

N/A = Not Available

*Includes base titration of benzoic acid initiator, where
used.

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TABLE IV

FTIR Spectra of PolyPIBSA

Sample- Product of Example No.	Molecular Weight	FTIR Frequency (cm ⁻¹)
2	5,000	1779.7
3	1,700	1781.2
4	1,350	1782.8
5	6,600	1778.1
6	9,100	1777.3
7	11,000	1775.8
8	1,400	1781.2
9	1,200	1782.8
10	1,300	1782.8
11	1,900	1780.5
12	8,000	1778.1
13	1,350	N/A
1C	900	1789.8
2C	N/A ^a	1789.1
3C	900	1785.2
4C	950	1787.5
5C	950	1785.9
Thermal PIBSA (BP polyisobutene)		1793.0
Thermal PIBSA (Exxon polyisobutene)		1793.0
Chlorination PIBSA (Exxon polyisobutene)		1785.
Chlorination PIBSA (Commercial Product)		1785.

^a N/A = not available.

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TABLE VFTIR Spectra of Polysuccinimides

07	<u>Sample-Product of Example No.</u>	<u>FTIR Frequency (cm⁻¹)</u>
08		
09	18	1697.5
10	19	N/A
11	20	1699.2
12	21	1700.4
13	22	1699.4
14		
15	MS-Th (mono-succinimide-thermal PIBSA)	1705.1
16	BS-Th (bis-succinimide-chlorination PIBSA)	1707.0
17	MS-Cl (mono-succinimide-chlorination PIBSA)	1706.2
18	PS-Cl (polysuccinimide-chlorination PIBSA)	1705.1
19	CS-Cl (commercial succinimide-chlorination	
20	PIBSA)	1705.1
21		
22		
23	N/A = not available.	
24		
25		
26		
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TABLE VISequence VE Engine Test Results - Sludge

<u>Sample 0.1</u>	<u>Rocker Cover Sludge</u>	<u>Average Engine Sludge</u>
Reference A	1.2	3.8
Reference A	1.6	3.3
Reference B	8.6	8.9
Reference B	9.2	9.2
Oil with 3%		
Product of		
Example 18	9.2	9.3
Oil with 6%		
Product of		
Example 18	9.0	9.2

EXAMPLE 23Preparation of Ethylene Carbonate Treated Bis
TEPA Polysuccinimide with a High Degree of Polymerization

To a 2 liter 3-necked flask equipped with an overhead stirrer, condensor and nitrogen inlet tube was added 677.0 g polyPIBSA, prepared according to Example 33, with a high degree of polymerization and 950 molecular weight polybutene tail (SAP No. 64.4, 0.389 mol). To this was added 267 g Chevron 100N diluent oil. This was then heated to 120°C under nitrogen with stirring and 36.7 g TEPA (0.194 mol) was added rapidly. This was stirred for 4 hours at 160°C. A total of 5.8 cc. water was produced. This produced a

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01 bisTEPA polysuccinimide with a high degree of polymeri-
02 zation. Then the temperature was lowered to 80°C and
03 102.43 g ethylene carbonate was added (1.16 mol). This
04 amount was required so that two moles of ethylene carbonate
05 reacted with each basic nitrogen in the bisTEPA poly-
06 succinimide. The temperature was increased to 160°C for 4
07 hours. A total of 1004.51 g of product was produced. The
08 product had the following properties: Acid No. = 0.08 mg
09 KOH/g; %N = 1.23%; Alkalinity Value = 14.18 mg KOH/g; and
10 viscosity at 100°C = 901.2 Cst.

11 EXAMPLE 24

12 Preparation of Ethylene Carbonate Treated Bis TEPA 13 Polysuccinimide with a Low Degree of Polymerization

14 To a 2 liter 3-necked flask equipped with an overhead
15 stirrer, condensor and nitrogen inlet tube was added 497.0 g
16 polyPIBSA prepared according to Example 17B with a low
17 degree of polymerization and 950 molecular weight polybutene
18 tail (Saponification No. 85.8, 0.38 mol). To this was added
19 447 g Chevron 100N diluent oil. This was then heated to
20 120°C under nitrogen with stirring and 35.9 g TEPA (0.19
21 mol) was added rapidly. This was stirred for 4 hours at
22 160°C. A total of 5.9 cc. water was produced. This
23 produced a bisTEPA polysuccinimide with a low degree of
24 polymerization. Then the temperature was lowered to 80°C
25 and 100.32 g ethylene carbonate was added (1.14 mol). This
26 amount was required so that two moles of ethylene carbonate
27 reacted with each basic nitrogen in the bisTEPA polysucci-
28 nimide. The temperature was increased to 160°C for 4 hours.
29 A total of 1030.0 g of product was produced. The product
30 had the following properties: Alkalinity Value 14.0 mg
31 KOH/g.
32
33
34

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EXAMPLE 25Preparation of Borated Bis HPA Polysuccinimide
with a High Degree of Polymerization

To a 2 liter 3-necked flask equipped with an overhead stirrer, condensor and nitrogen inlet tube was added 864.0 g polyPIBSA made in a manner similar to Example 35, with a high degree of polymerization and 950 molecular weight polybutene tail (Saponification No. 49.0, 0.38 mol). To this was added 121 g Chevron 100N diluent oil. This was then heated to 140°C under nitrogen with stirring and 52.3 g HPA (0.19 mol) was added rapidly. This was stirred for 4 hours at 170°C. A total of 7.5 cc. water was produced. This produced a bisHPA polysuccinimide with a high degree of polymerization. Then the temperature was lowered to 65°C and 50 cc water and 27.09 g boric acid (0.44 mol) was added. This was heated at reflux (102°C) for 2 hours, then the water was removed by distillation. The temperature was then increased to 171°C for 2.5 hours. Then the product was decanted. The product had the following properties: Acid No. = 2.30 mg KOH/g; %N = 1.68%; %Boron = 0.53; and viscosity at 100°C = 1014 Cst. It is anticipated that this borated product will have improved wear properties.

EXAMPLE 26Preparation of Borated Bis TEPA
Polysuccinimide with a Low Degree of Polymerization

To a 2 liter 3-necked flask equipped with an overhead stirrer, condensor and nitrogen inlet tube was added 500 g polysuccinimide from Example 46. This was then heated to 50°C under nitrogen with stirring and 50 ml water and 28.2 g boric acid (0.45 mol) was added. This was then heated at

63

01 reflux (102°C) for 2 hours. Then the water was distilled
02 off, and the temperature was increased to 165°C for 1.5
03 hours. A total of 517.0 g of product was produced. The
04 product had the following properties: $\eta_N = 1.24$; viscosity
05 at 100°C = 312.5 Cst; Acid No. = 24.3 and $\eta_B = 1.01\%$. It is
06 anticipated that this borated product will have improved
07 wear properties.

08
09 EXAMPLES 27 to 36

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11 Table VII includes the results from additional preparations
12 of polyPIBSA that were carried out using the basic synthetic
13 procedure outlined in Examples 1 and 2. Table VII lists the
14 reactants, reaction temperature, time and solvent and free
15 radical initiator used as well as the weight of product and
16 the saponification value.

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TABLE VII

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator (g)	Temp. °C	Time hrs	Weight Product (g)	Saponification value mg KOH/g Sample
27	Ultrasvis-10 (330)	32.34	chlorobenzene (210)	TBPB (1.2)	138	30	345	51
28	Ultrasvis-10 (330)	32.34	chlorobenzene (210)	TBPB (0.6)	138	30	331	38
29	Ultrasvis-30 (2171)	164	dichloroethane (1050)	TBPB (33)	83	23	2265	55
30	Ultrasvis-30 (4147)	328	chlorobenzene (1600)	DTBP (42.6)	142	20	4429	67
31	Ultrasvis-30 (4342)	328	dichloroethane (2000)	TBPB (66)	83	22	4633	47
32	Ultrasvis-10 (5000)	515.8	dichloroethane (3000)	DTBP (77.4)	90	42	5506	46
33	Ultrasvis-10 (5000)	515.8	dichloroethane (3000)	DTBP (77.4)	91	92	5339	64.4

TBPB = t-butylperoxybenzoate
DTBP = dit-butyl peroxide

65

TABLE VII (continued)

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator (g)	Temp. °C	Time hrs	Weight Product (g)	Saponification valve mg KOH/g Sample
34	Ultrasvis-30 (5000)	376.9	dichloroethane (3000)	DTBP (56.2)	91	92	5350	34
35	Ultrasvis-10 (2000)	205.88	dichloroethane (1200)	EDTBPB (96.8)	91	29	2100	51
36	Ultrasvis-30 (6000)	453	dichloroethane (3000)	TBPO (149.91)	91	24	6272	50

DTBP = dit-butyl peroxide
TBPO = t-butyl peroctanoate
EDTBPB = ethyl -3,3-di(t-butyl peroxy)butyrate

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01

EXAMPLES 37 to 48

02

03 Table VIII includes the results from additional preparations
04 of polysuccinimides that were carried out using the basic
05 synthetic procedure outlined in Examples 18-22. Table VIII
06 lists the polyPIBSA used, the amount of diluent oil added,
07 the polyamine used, the calculated charge mol ratio (CMR),
08 the weight of final product, the water produced, and the %N.

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TABLE VIII

Example	PolyPIBSA Used (g)	Diluent Oil (g)	Polyamine Used (g)	CHR	Wt. of Product (g)	%N	ml H ₂ O Produced
37	Example 17B (500)	443.9	HPA (93.6)	0.89	1025.7	2.94	6.2
38	Example 17B (1000)	1019	TETA (55.8)	0.5	2122.6	0.99	9.1
39	Example 15 *(1280)	696	TETA (99.3)	0.89	2060	1.79	15.0
40	Example 31 **(1949)	72	TETA (55.8)	0.5	1965.2	0.98	12
41	Example 32 (1776.8)	1881	HPA (104.5)	0.5	3740	0.92	13
42	Example 35 (1423.0)	690	TETA (110.96)	0.89	2200	1.8	16.5
43	Example 35 (1273)	1697	HPA (104.5)	0.5	3060	1.13	14
44	Example 31 (1403.6)	500	HPA (75.21)	0.5	1965	2.14	13
45	Example 36 (500)	109	HPA (28.88)	0.5	606.3	1.50	3.6

*In this example, extra diluent oil (36%) was added to the polyPIBSA to make it easier to filter.

**In this example, extra diluent oil (18.4%) was added to the polyPIBSA to make it easier to filter.

TABLE VIII (continued)

Example	Polypibsa Used (g)	Diluent Oil (g)	Polyamine Used (g)	CHR	Wt. of Product (g)	XN	ml H ₂ O Produced
46	Example 17B (2500)	2248	TEPA (180.59)	0.5	4879.2	1.4	31
47	Example 35 (458)	26.7	TEPA (18.9)	0.5	501.79	1.2	3.6
48	Example 17B (261.62)	209.11	TEPA (32.89)	0.87%	497.34	2.2	2.6

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EXAMPLE 49

02

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Viton Seal Swell Test

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05 Some lubricating oil additives have been identified as being
06 deleterious to fluoroelastomers such as Viton that are
07 currently used as gasket materials in automobile engines.
08 European engine builders have now placed fluoroelastomer
09 seal tests into their engine oil specifications. One such
10 test is the Volkswagen VW3334 (September 1987) Seal Swell
11 Test. This procedure is described in the Third Symposium of
12 the European Coordination Council (CEC) 1989 in an article
13 entitled "Engine and Bench Aging Effects on the
14 Compatibility of Fluoroelastomers with Engine Oils" by
15 Dr. S. W. Harris and J. C. Downey of Amoco Petroleum
16 Additives Company.

17

18 The VW3334 (September 1987) Seal Swell Test was carried out
19 on samples of Viton from the Parker Prudifa Company which
20 were cut into dumbbell shapes, using a formulated
21 lubricating test oil that contained succinimide dispersant,
22 overbased detergent, antioxidant and viscosity index
23 improver materials at a bath temperature of 150°C for a 96
24 hour immersion time. The immersion procedure was similar to
25 ASTM D471-79 Standard Test Method for Rubber Property-Effect
26 of Liquids. Commercial succinimide dispersants were
27 compared to the polysuccinimides of present Examples 47 and
28 48. The Viton samples were then subjected to analysis of
29 their tensile properties using procedures similar to ASTM
30 D412-87 Standard Test Method for Rubber Properties in
31 Tension. The properties that were measured were cracking at
32 120 percent elongation, percent change in tensile strength
33 and percent change in elongation at break, in accordance

34

01 with the VW3334 Seal Swell Test requirements. The results
02 are shown in Table IX.

03

04 The data in Table IX demonstrates that the polysuccinimide
05 of Example 47 passed the Viton Seal Swell Test at the 0.07%
06 nitrogen level, whereas the commercial bis-succinimide
07 failed. Although the polysuccinimide of Example 48 did not
08 pass the Viton test at the 0.13% nitrogen level, it
09 performed better in this test than the commercial mono-
10 succinimide at the 0.12% nitrogen level.

11

12

TABLE IX

13

14

VITON SEAL SWELL TEST

15

16	<u>Sample</u>	<u>Ts</u> ¹	<u>El</u> ²	<u>Cr</u> ³	<u>%N</u>
17					
18	Commercial monosuccinimide	-54	-43	Yes	0.12
19	Polysuccinimide, Example 48	-49	-39	Yes	0.13
20	Commercial bis-succinimide	-29	-23	No	0.07
21	Polysuccinimide, Example 47	-15	-17	No	0.07
22					
23	passing limit	±20	±25	No	

24

25

26 ¹Tensile strength & change

27 ²Elongation to break & change

28 ³Cracks, yes or no at 120% elongation

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EXAMPLE 50

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02

03 This example shows that after the copolymer of the present
04 invention is formed, unreacted polybutene can be reacted
05 with maleic anhydride to form thermal process PIBSA.

06

07 PolyPIBSA prepared in a manner similar to Example 17B having
08 a Saponification No. of 86 was charged to a reactor and
09 heated to 204°C. A molar equivalent of maleic anhydride
10 (43.3 g), relative to unreacted non-vinylidene polybutene,
11 was added and the mixture heated to 232°C and held at this
12 temperature for 4 hours. The temperature was reduced to
13 210°C and the pressure was reduced to 28 inches of mercury.
14 The reduced pressure and temperature was maintained for one
15 hour. Then the mixture was filtered. The product had a
16 Saponification No. of 88.

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01 WHAT IS CLAIMED IS:

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03 1. A copolymer of an unsaturated acidic reactant and a
04 high molecular weight olefin having a sufficient number
05 of carbon atoms such that the resulting copolymer is
06 soluble in lubricating oil and wherein at least 20
07 percent of the total olefin comprises an
08 alkylvinylidene isomer.

09

10 2. A copolymer according to Claim 1 wherein at least 50
11 percent of the total olefin comprises an
12 alkylvinylidene isomer.

13

14 3. A copolymer according to Claim 2 wherein said
15 unsaturated acidic reactant is of the formula:

16

17

18



19

20 wherein X and X' are each independently selected from
21 the group consisting of -OH, -Cl, -O-lower alkyl and
22 when taken together, X and X' are -O-.

23

24 4. A copolymer according to Claim 3 having an average
25 degree of polymerization greater than 1.0.

26

27 5. A copolymer according to Claim 4 wherein said olefin
28 has an average molecular weight of about 500 to about
29 5000.

30

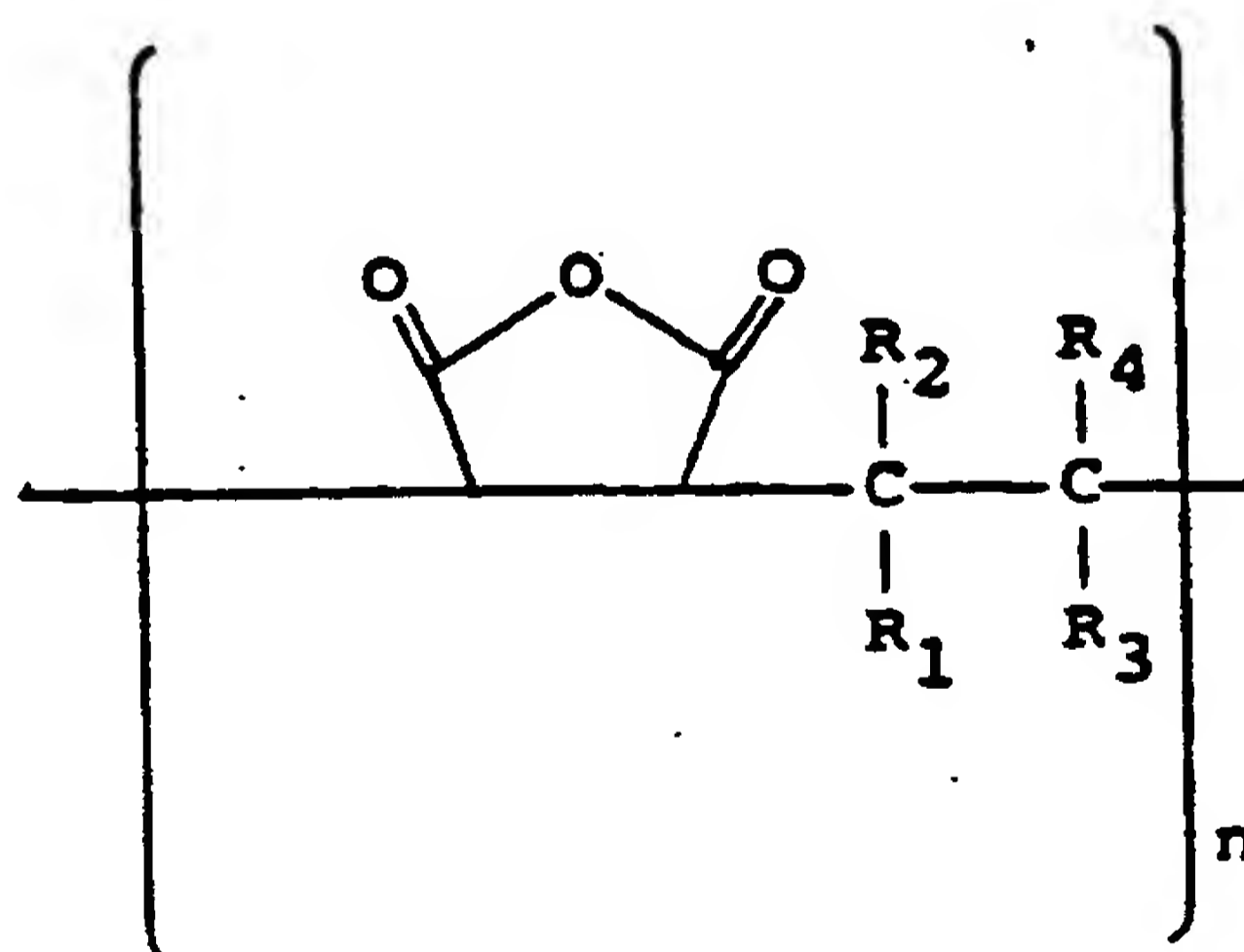
31 6. A copolymer according to Claim 5 wherein said olefin is
32 polyisobutene.

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- 01 7. A copolymer according to Claim 6 having an average
 02 degree of polymerization of about 1.5 to about 10.
 03
- 04 8. A copolymer according to Claim 7 wherein said acidic
 05 reactant comprises maleic anhydride.
 06
- 07 9. A copolymer according to Claim 8 wherein said
 08 polyisobutene has an average molecular weight of about
 09 900 to about 2500.
 10
- 11 10. A copolymer according to Claim 9 wherein at least about
 12 70 percent of the total olefin comprises an
 13 alkylvinylidene isomer.
 14
- 15 11. A copolymer according to Claim 10 wherein said
 16 alkylvinylidene isomer is methylvinylidene.
 17
- 18 12. A copolymer of the formula:
 19
 20



31 wherein n is 1 or greater, and R₁, R₂, R₃ and R₄ are
 32 selected from hydrogen, lower alkyl of 1 to 6 carbon
 33 atoms and high molecular weight polyalkyl; wherein
 34

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- 01 either R_1 and R_2 are hydrogen and one of R_3 and R_4 is
02 lower alkyl and the other is high molecular weight
03 polyalkyl, or R_3 and R_4 are hydrogen and one of R_1 and
04 R_2 is lower alkyl and the other is high molecular
05 weight polyalkyl.
06
- 07 13. A copolymer according to Claim 12 wherein said high
08 molecular weight polyalkyl comprises a polyisobutyl
09 group of at least about 50 carbon atoms.
10
- 11 14. A copolymer according to Claim 13 wherein said
12 polyisobutyl group has an average molecular weight of
13 about 500 to 5000.
14
- 15 15. A copolymer according to Claim 14 wherein said
16 polyisobutyl group has an average molecular weight of
17 about 900 to 2500.
18
- 19 16. A copolymer according to Claim 15 wherein having an
20 average degree of polymerization of about 1.1 to about
21 20.
22
- 23 17. A copolymer according to Claim 16 wherein said lower
24 alkyl is methyl.
25
- 26 18. A product prepared by the process which comprises
27 reacting a higher molecular weight olefin wherein at
28 least about 20 percent of the total high molecular
29 weight olefin comprises an alkylvinylidene isomer and
30 wherein said high molecular weight olefin has a
31 sufficient number of carbon atoms that said product is
32 soluble in lubricating oil with an unsaturated acidic
33 reactant in the presence of a free radical initiator.
34

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- 01 19. A product prepared as in the process of Claim 18
02 wherein said unsaturated acidic reactant is of the
03 formula:



- 07 wherein X and X' are each independently selected from
08 the group consisting of -OH, -Cl, -O-lower alkyl and
09 when taken together, R and R' are -O-.

- 10
11 20. A product prepared as in the process of Claim 19
12 wherein at least 50 percent of the total olefin
13 comprises an alkylvinylidene isomer.

- 14
15 21. A product prepared as in the process of Claim 20
16 wherein said high molecular weight olefin has an
17 average molecular weight of about 500 to about 5000.

- 18
19 22. A product prepared as in the process of Claim 21
20 wherein said high molecular weight olefin is
21 polyisobutene.

- 22
23 23. A product prepared as in the process of Claim 22 having
24 an average degree of polymerization of about 1.5 to
25 about 10.

- 26
27 24. A product prepared as in the process of Claim 23
28 wherein said acidic reactant is maleic anhydride and
29 said alkylvinylidene isomer is methylvinylidene.

- 30
31 25. A copolymer according to Claim 1, 6 or 11 having a
32 characteristic infrared succinic anhydride stretch in
33 the range of about 1775 cm^{-1} to about 1784 cm^{-1} as
34 measured by infrared spectroscopy.

- 01 26. A polysuccinimide prepared by reacting a copolymer
02 according to Claim 1, 6 or 11 with a polyamine having
03 at least one basic nitrogen atom.
04
05
- 06 27. A polysuccinimide according to Claim 26 having a
07 characteristic infrared succinimide stretch in the
08 range of about 1697 cm^{-1} to about 1703 cm^{-1} as measured
09 by infrared spectroscopy.
10
- 11 28. A polysuccinimide according to Claim 26 wherein said
12 polyamine has from about 2 to about 12 amine nitrogen
13 atoms and from about 2 to about 40 carbon atoms.
14
- 15 29. A polysuccinimide according to Claim 28 wherein said
16 polyamine has the formula $\text{H}_2\text{N}(\text{YNH})_p\text{H}$ wherein Y is
17 alkylene of 2 to 6 carbon atoms and p is an integer
18 from 1 to 6.
19
- 20 30. A polysuccinimide according to Claim 29 wherein the
21 charge mole ratio of polyamine to succinic groups in
22 copolymer is from about 1 to about 0.1.
23
- 24 31. A polysuccinimide according to Claim 29 wherein the
25 charge mole ratio of polyamine to succinic groups in
26 copolymer is about 0.5.
27
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01 32. A compound of the formula:

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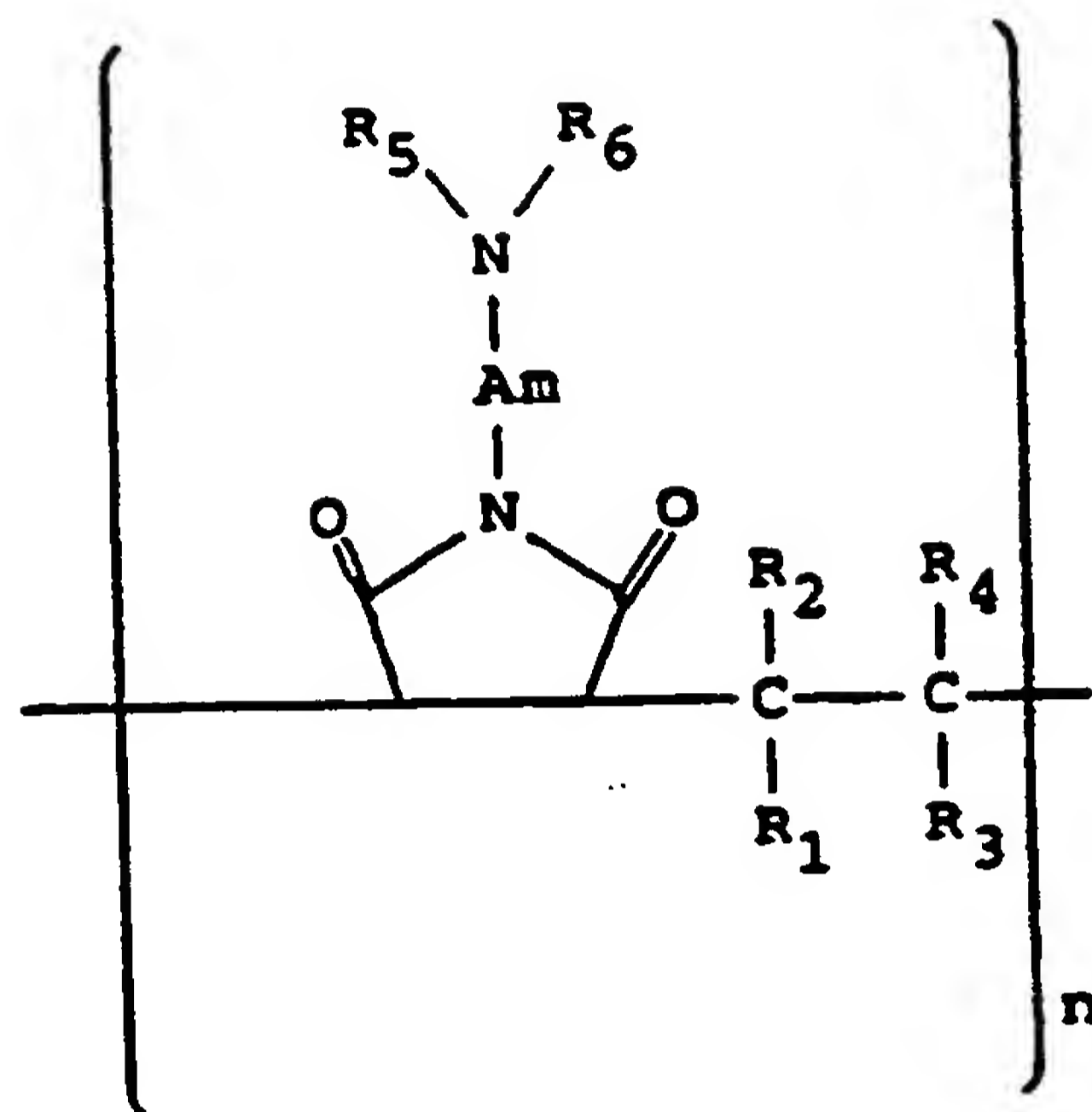
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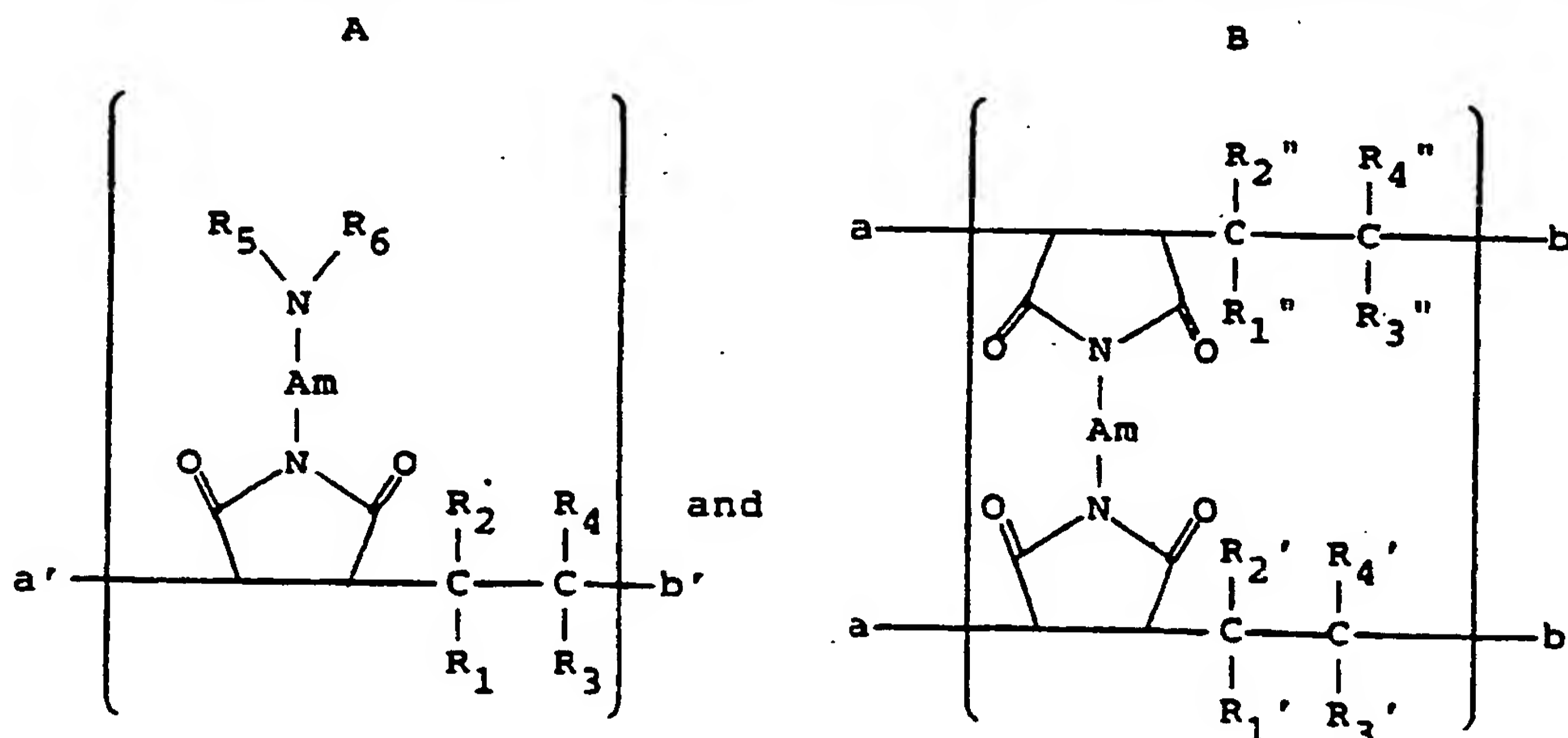


wherein n is one or greater, Am has from about 0 to about 10 amine nitrogen atoms and from about 2 to about 40 carbon atoms; and R₁, R₂, R₃ and R₄ are selected from hydrogen, lower alkyl of 1 to 6 carbon atoms and high molecular weight polyalkyl; wherein either R₁ and R₂ are hydrogen and one of R₃ and R₄ is lower alkyl and the other is high molecular weight polyalkyl, or R₃ and R₄ are hydrogen and one of R₁ and R₂ is lower alkyl and the other is high molecular weight polyalkyl; and R₅ and R₆ are independently hydrogen, lower alkyl of 1 to 6 carbon atoms, phenyl or taken together are alkylene of 3 to 6 carbon atoms to give a ring.

33. A compound according to Claim 32 wherein said high molecular weight polyalkyl comprises a polyisobutyl group of at least about 50 carbon atoms.

34. A compound according to Claim 33 wherein said polyisobutyl group has an average molecular weight of about 500 to about 5000.

- 01 35. A compound according to Claim 34 wherein Am has the
 02 formula $[(ZNH)pZ']$ wherein Z and Z' are independently
 03 alkylene of from 2 to 6 carbon atoms and p is an
 04 integer from 1 to 6, and R_5 and R_6 are hydrogen.
 05
- 06 36. A compound according to Claim 35 having an average
 07 degree of polymerization of about 1.1 to about 20.
 08
- 09 37. A compound according to Claim 36 wherein said
 10 polyisobutyl group has an average molecular weight of
 11 about 900 to about 2500.
 12
- 13 38. A compound according to Claim 37 wherein said lower
 14 alkyl is methyl.
 15
- 16 39. A compound according to Claim 38 having an average
 17 degree of polymerization of about 1.5 to about 10.
 18
- 19 40. A compound according to Claim 37 wherein Z and Z' are
 20 ethylene and p is 2, 3 or 4.
 21
- 22 41. A random polysuccinimide comprising units selected from



- 01
02 wherein Am is a linking group having from about 0 to 10
03 amine nitrogen atoms and from about 2 to 40 carbon
04 atoms; R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , R_4' , R_1'' , R_2'' ,
05 R_3'' , and R_4'' are selected from hydrogen, lower alkyl of
06 one to 6 carbon atoms and high molecular weight poly-
07 alkyl; wherein either R_1 and R_2 are hydrogen and one of
08 R_3 and R_4 is lower alkyl and the other is polyalkyl, or
09 R_3 and R_4 are hydrogen and one of R_1 and R_2 is lower
10 alkyl and the other is polyalkyl; either R_1' and R_2'
11 are hydrogen and one of R_3 and R_4 is lower alkyl and
12 the other is polyalkyl, or R_3' and R_4' are hydrogen and
13 one of R_1' and R_2' is lower alkyl and the other is
14 polyalkyl; and either R_1'' and R_2'' are hydrogen and one
15 of R_3'' and R_4'' is lower alkyl and the other is poly-
16 alkyl or R_3'' and R_4'' are hydrogen and one of R_1'' and
17 R_2'' is lower alkyl and the other is polyalkyl; R_5 and
18 R_6 are independently hydrogen, lower alkyl of 1 to 6
19 carbon atoms, phenyl or taken together are alkylene of
20 3 to 6 carbon atoms to give a ring; and a, a', b and b'
21 are sites for a covalent bond; provided that at least
22 one a or a' site of each unit is covalently bonded to a
23 b or b' site.
24
- 25 42. A random polysuccinimide according to Claim 41 wherein
26 said high molecular weight polyalkyl comprises a
27 polyisobutyl group of at least about 50 carbon atoms.
28
- 29 43. A random polysuccinimide according to Claim 42 wherein
30 said polyisobutyl group has an average molecular weight
31 of about 500 to 5000.
32
- 33 44. A random polysuccinimide according to Claim 43 wherein
34 Am has the formula $-[(ZNH)_pZ']-$ wherein Z is alkylene

- 01 of 2 to 6 carbon atoms, z' is alkylene of 2 to 6 carbon
02 atoms and p is an integer from 0 to 5, and R_5 and R_6
03 are hydrogen.
04
- 05 45. A random polysuccinimide according to Claim 44 wherein
06 the average sum of A and B units is from about 2 to
07 about 50.
08
- 09 46. A random polysuccinimide according to Claim 45 wherein
10 said polyisobutyl group has an average molecular weight
11 of about 900 to about 2500.
12
- 13 47. A random polysuccinimide according to Claim 46 wherein
14 said lower alkyl is methyl.
15
- 16 48. A random polysuccinimide according to Claim 47
17 comprising from about 2 to about 10 times as many B
18 units as A units.
19
- 20 49. A random polysuccinimide according to Claim 48 wherein
21 z and z' are ethylene and p is 1, 2 or 3.
22
- 23 50. A fuel composition comprising a hydrocarbon boiling in
24 a gasoline or diesel range and from about 30 to about
25 5000 parts per million of a copolymer according to
26 Claim 11.
27
- 28 51. A fuel composition comprising a hydrocarbon boiling in
29 a gasoline or diesel range and from about 30 to about
30 5000 parts per million of an polysuccinimide according
31 to Claim 29.
32
- 33 52. A fuel composition comprising a hydrocarbon boiling in
34 a gasoline or diesel range and from about 30 to about

81

- 01 5000 parts per million of an compound according to
02 Claim 40.
03
- 04 53. A fuel composition comprising a hydrocarbon boiling in
05 a gasoline or diesel range and from about 30 to about
06 5000 parts per million of an random polysuccinimide
07 according to Claim 49.
08
- 09 54. A fuel concentrate comprising an inert stable
10 oleophilic organic solvent boiling in the range of
11 150°F to 400°F and from about 5 to about 50 weight
12 percent of a copolymer according to Claim 11.
13
- 14 55. A fuel concentrate comprising an inert stable
15 oleophilic organic solvent boiling in the range of
16 150°F to 400°F and from about 5 to about 50 weight
17 percent of a polysuccinimide according to Claim 29.
18
- 19 56. A fuel concentrate comprising an inert stable
20 oleophilic organic solvent boiling in the range of
21 150°F to 400°F and from about 5 to about 50 weight
22 percent of a compound according to Claim 40.
23
- 24 57. A fuel concentrate comprising an inert stable
25 oleophilic organic solvent boiling in the range of
26 150°F to 400°F and from about 5 to about 50 weight
27 percent of a random polysuccinimide according to
28 Claim 49.
29
- 30 58. A lubricating oil composition comprising an oil of
31 lubricating viscosity and a dispersant effective amount
32 of a copolymer according to Claim 11.
33
34

- 01 59. A lubricating oil composition comprising an oil of
02 lubricating viscosity and a dispersant effective amount
03 of a polysuccinimide according to Claim 29.
04
- 05 60. A lubricating oil composition comprising an oil of
06 lubricating viscosity and a dispersant effective amount
07 of a compound according to Claim 40.
08
- 09 61. A lubricating oil composition comprising an oil of
10 lubricating viscosity and a dispersant effective amount
11 of a random polysuccinimide according to Claim 49.
12
- 13 62. A lubricating oil concentrate comprising from about 90
14 to about 50 weight percent of an oil of lubricating
15 viscosity and from about 10 to about 50 weight percent
16 of a copolymer according to Claim 11.
17
- 18 63. A lubricating oil concentrate comprising from about 90
19 to about 50 weight percent of an oil of lubricating
20 viscosity and from about 10 to about 50 weight percent
21 of a polysuccinimide according to Claim 29.
22
- 23 64. A lubricating oil concentrate comprising from about 90
24 to about 50 weight percent of an oil of lubricating
25 viscosity and from about 10 to about 50 weight percent
26 of a compound according to Claim 40.
27
- 28 65. A lubricating oil concentrate comprising from about 90
29 to about 50 weight percent of an oil of lubricating
30 viscosity and from about 10 to about 50 weight percent
31 of a random polysuccinimide according to Claim 49.
32
- 33 66. A product prepared by the process which comprises
34 reacting a polysuccinimide according to Claim 26 having

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- 01 at least one primary or secondary amine group with a
02 cyclic carbonate or a linear mono- or poly-carbonate.
03
- 04 67. The product according to Claim 66, wherein the
05 polysuccinimide is reacted with a cyclic carbonate.
06
- 07 68. The product according to Claim 67, wherein the cyclic
08 carbonate is ethylene carbonate.
09
- 10 69. A product prepared by the process which comprises
11 reacting a polysuccinimide according to Claim 26 with a
12 boron compound selected from the group consisting of
13 boron oxide, boron halide, boric acid and esters of
14 boric acid.
15
- 16 70. The product according to Claim 69, wherein the boron
17 compound is boric acid.
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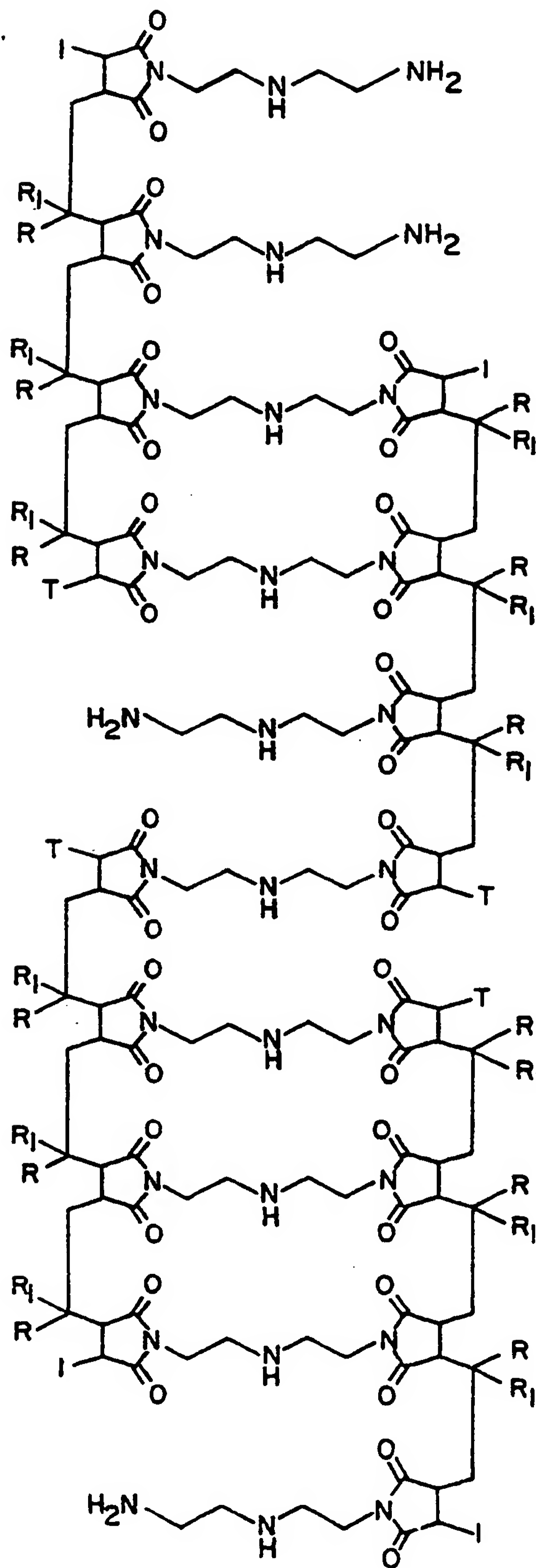


FIG. 1.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04270

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC INT CL4: C07C 55/00,69/34; C07D,307/34; C10M 129/93; C10L 1/18,1/22 US CL: 562/590,596; 560/190,204; 549/233,252; 526/262; 548/546,547; 252/56D,51.5A 44/62 ⁶³																							
II. FIELDS SEARCHED Minimum Documentation Searched ? <table border="1"> <tr> <th>Classification System</th> <th>Classification Symbols</th> </tr> <tr> <td>US</td> <td>562/590,596; 560/190,204; 549/233,252; 526/262; 548/546,547; 252/56D,51.5A; 44/62,63</td> </tr> </table> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *			Classification System	Classification Symbols	US	562/590,596; 560/190,204; 549/233,252; 526/262; 548/546,547; 252/56D,51.5A; 44/62,63																	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT * <table border="1"> <tr> <th>Category *</th> <th>Citation of Document, ** with Indication, where appropriate, of the relevant passages 12</th> <th>Relevant to Claim No. 13</th> </tr> <tr> <td>X Y</td> <td>US, A, 4,548,725, (BRIDGER) 22 October 1985 See entire document</td> <td>1-8,12,14,18-23, 25,58,62,16 9-11,13,15,17,24</td> </tr> <tr> <td>X Y</td> <td>US, A, 4,526,950, (GRAVA) 02 July 1985 See entire document</td> <td>1-4,8,10,12,16,18- 20,23,25,7 5,6,9,11,13-15,17 21,22,24</td> </tr> <tr> <td>X Y</td> <td>US, A, 4,416,668, (THOMPSON) 22 November 1983 See entire document</td> <td>26-36,39,40,51, 52,55,56 37,38</td> </tr> <tr> <td>X Y</td> <td>US, A, 3,677,725, (ANDRESS, JR) 18 July 1972 See entire document</td> <td>1-4,7,8,12,16,18- 20,23,25,50,54 5,6,9-11,13-15,17 21,22,24</td> </tr> <tr> <td>X Y P</td> <td>JP, A, 63-270671, (MITSUBISHI) 08 Novmeber 1988 See entire document</td> <td>1-8,12-14,16,18- 23,25,58,62 9-11,15,17,24</td> </tr> <tr> <td>A</td> <td>US, A, 4,612,132 (WOLLENBERG ET AL) 16 September 1986, See entire document</td> <td>66,67,68</td> </tr> </table>			Category *	Citation of Document, ** with Indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13	X Y	US, A, 4,548,725, (BRIDGER) 22 October 1985 See entire document	1-8,12,14,18-23, 25,58,62,16 9-11,13,15,17,24	X Y	US, A, 4,526,950, (GRAVA) 02 July 1985 See entire document	1-4,8,10,12,16,18- 20,23,25,7 5,6,9,11,13-15,17 21,22,24	X Y	US, A, 4,416,668, (THOMPSON) 22 November 1983 See entire document	26-36,39,40,51, 52,55,56 37,38	X Y	US, A, 3,677,725, (ANDRESS, JR) 18 July 1972 See entire document	1-4,7,8,12,16,18- 20,23,25,50,54 5,6,9-11,13-15,17 21,22,24	X Y P	JP, A, 63-270671, (MITSUBISHI) 08 Novmeber 1988 See entire document	1-8,12-14,16,18- 23,25,58,62 9-11,15,17,24	A	US, A, 4,612,132 (WOLLENBERG ET AL) 16 September 1986, See entire document	66,67,68
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* Special categories of cited documents: 10 "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family																							
IV. CERTIFICATION <table border="1"> <tr> <td>Date of the Actual Completion of the International Search 12 December 1989</td> <td>Date of Mailing of this International Search Report 10 JAN 1990</td> </tr> <tr> <td>International Searching Authority ISA/US</td> <td>Signature of Authorized Officer <i>Allen McAlister</i></td> </tr> </table>			Date of the Actual Completion of the International Search 12 December 1989	Date of Mailing of this International Search Report 10 JAN 1990	International Searching Authority ISA/US	Signature of Authorized Officer <i>Allen McAlister</i>																	
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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US,A, 4,359,325, (DAWANS ET AL) 16 November 1982 See entire document	1-70
A	US,A, 4,055,581, (HOPKINS ET AL) 25 October 1977 See entire document	1-70
A	US,A, 3,720,733, (RINKLER ET AL) 13 March 1973 See entire document	1-70
A	US,A, 2,977,334, (ZOPF, JR ET AL) 28 March 1961 See entire document	1-70
A	SU,A, 900,599, (A MED POLIO VIRUS) 15 January 1985 See entire document	1-70

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the International application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING³

This International Searching Authority found multiple inventions in this International application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this International search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

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